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OF
THE CHEMICAL SOCIETY.

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1923. Vol. CXXIII. Part I, pp. 1-1647.

LONDON:

GURNEY & JACKSON, 33, PATERNOSTER ROW, E.C. 4.
1923.

PRINTED IN GREAT BRITAIN BY
RICHARD CLAY & SONS, LIMITED,
BUNGAY, SUFFOLK.

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JOURNAL
OF
THE CHEMICAL SOCIETY.
TRANSACTIONS.

I.—*Investigations on the Dependence of Rotatory Power on Chemical Constitution. Part XIII.* The Spatial Configuration of the Unbranched Aliphatic Chain.*

By ROBERT HOWSON PICKARD, JOSEPH KENYON, and HAROLD HUNTER.

ADOPTING the accepted view that the carbon atom may be considered as a sphere with its four valencies directed mainly to the vertices of an inscribed tetrahedron, Frankland (T., 1899, 75, 368) suggested that a chain of such atoms might be expected to form a spiral which would complete one turn at about the fifth member, and that we should accordingly look for anomalies in physical properties at that point. Attention must be directed to the fact, however, that the spiral is by no means the only form which the chain can assume, nor, considered solely on mathematical grounds, is it the most probable. For, after the third member, there are three possible directions in space for extension of the chain to take place, only one of which will lead to the spiral configuration. This is the case at each additional member after the third, and therefore the probability of a chain of such atoms assuming a spiral form as a result of pure chance is at most $1/3^{n-3}$, where n is the number of atoms in the chain. That is to say, for a four-membered chain the odds are at least 2 to 1 against, for a

* In this paper references are made to Part I, T., 1911, 99, 45; Part II, E., 1912, 101, 629; Part III, *ibid.*, 1427; Part V, E., 1914, 105, 830; Part VII, *ibid.*, 2226; Part VIII, *ibid.*, 2262; Part IX, *ibid.*, 2644; Part XI, T., 1915, 107, 115.

five-membered chain they are 8 to 1 against, and for a thirteen-membered chain they are 60,000 to 1 against such a form being assumed as a result of pure chance.

A review of our previous work bearing on this point shows that Frankland's conception of the spiral chain may now be extended to include some heterocatenic substances in which one atom of oxygen is included in the chain.

It has been shown in the earlier parts of these investigations that the optical rotatory powers of members of many homologous series vary in a regular manner with molecular weight. In view of what has been said above, then, it is a fact of great significance that this regularity is often disturbed at perfectly definite points in the series, after which the normal variation is resumed until the next point is reached, and so on. These points occur when an unbranched chain of carbon (or carbon and oxygen) atoms contains five (or a multiple of five) members. Occasionally this effect is noticed at the points where the chain contains six or eleven atoms, but in this connexion it must be remembered that the valency directions of the carbon atom are not invariably inclined at an angle of $109^{\circ} 28'$ to each other as the conception of rigid bonds by van't Hoff and by Baeyer would lead us to expect. Rather is it the case, as Ingold and his colleagues (T., 1921, **119**, 305, *et seq.*) have recently shown, that the angle between the valency directions of the carbon atom depends on the volumes of the atoms or groups to which it is attached. Thus the normal angle between the carbon-to-carbon valencies in a polymethylene chain is not 109.5° , but 115.3° , and therefore there will be more atoms in one complete turn of the spiral in the case of an unsubstituted polymethylene chain than in the case of a substituted chain. Then, again, in the case of the oxygen atom, we are not certain of the directions in which its valencies mainly act. Its volume is almost identical with that of the carbon atom: it frequently—much more frequently than was formerly supposed—exercises quadrivalency and may therefore perhaps be regarded as nearly identical with the carbon atom so far as its influence on the configuration of a chain is concerned. But it would require only a slight change of the "intervalent" angle to modify the shape of the chain sufficiently to cause irregularities to appear at the sixth or eleventh instead of the fifth and tenth members of a series, and either of the above causes would be amply sufficient to determine such a change.

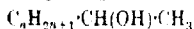
Up to the present, marked irregularities in the numerical value of a physical property in a homologous series at points where a spiral chain may be assumed to have completed an integral number of turns have been detected only in rotatory power. Similar

irregularities, although much less in amount, have, however, been observed in the densities of members of homologous series, for example, in the isopropyl-*n*-alkylcarbinols (Part II, p. 637), the esters of ac-tetrahydro- β -naphthol (Part III, p. 1430), the ethyl-*n*-alkylcarbinols (Part IV, p. 1935), and the esters of isopulgol (T., 1920, 117, 1248). In the last case this irregularity is reflected in the values of the molecular refractive power (R_L^D). These other irregularities are, however, very small in amount, being often very little greater than the experimental error, and it would be rash to base conclusions on consideration of these alone. But as confirmatory evidence they are helpful, although we are forced to the conclusion that it is the highly constitutive nature of optical activity which renders it so pre-eminently useful in the elucidation of the finer details of molecular architecture.

Some of the cases of abnormality of rotatory power associated with the presence within the molecule of a chain containing five, ten, or fifteen atoms of carbon or of carbon and oxygen may now be discussed.

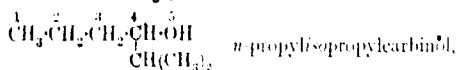
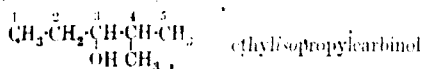
In the homologous series of methyl-*n*-alkylcarbinols (Part I, p. 49), the rotatory power at 20° in the homogeneous state of the propyl member is abnormally high compared with those of the rest of the series. This abnormality is intensified at 10°. When the rotatory powers are determined in solution in benzene and in ethyl alcohol (Part VI, p. 1928), in addition to the abnormality at the propyl member, we find similar ones at the amyl, octyl, and decyl members.

Representing the series by the general formula



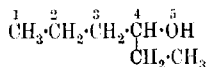
we see that when $n = 5$ or a multiple thereof, the growing chain attached to the asymmetric carbon atom will have completed one or more turns of the spiral. When, on the other hand, n is two less than 5 or a multiple thereof, the whole chain of carbon atoms in the molecule will have made one or more complete turns of the spiral.

The temperature-rotation curves for the ethyl and *n*-propyl members of the alkylisopropylcarbinols (Part II, p. 623) are similar to each other and differ from those of the rest of the series. Writing down the formulæ of these alcohols



it is immediately obvious that in the former case we have a chain of five carbon atoms, and in the latter, one of four carbon and one oxygen atom.

Again, ethyl-*n*-propylcarbinol (Part VI, p. 1924),

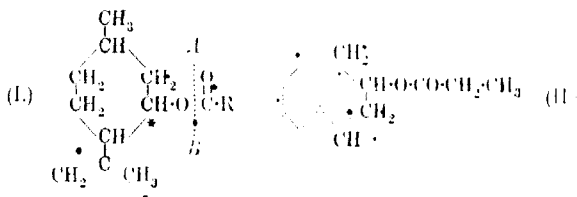


has a low rotation compared with the other ethylalkylcarbinols—it may be that this is due to the chain of one oxygen and four carbon atoms in the molecule.

Perhaps the most striking example of these irregularities is to be found in the series of ethylalkylcarbinols (Part IV). If the specific rotatory powers of these alcohols be plotted as ordinates with the number of carbon atoms in the growing alkyl chain as abscissæ, it is found that the *n*-amyl and *n*-hexyl and again the *n*-decyl, *n*-undecyl, and *n*-dodecyl members have rotatory powers considerably in excess of what may be regarded as the normal value deduced from considerations of the rotatory powers of the other members of the series. Here again we see the influence of a chain of five and six and also ten and eleven carbon atoms, and in this particular case the rotations are measured in the homogeneous state, so that we do not have to consider the effect of solution, which is at present very little understood.

The effect of solvent and also of change of temperature on these irregularities is exemplified in the series of esters of *L*-isopulegol (T., 1920, 117, 1248). Measured in the homogeneous state at 20°, the specific rotatory powers of these esters show a regular decrease, after the first three members, in their numerical value. This regularity is sharply interrupted at the *n*-valerate and again at the *n*-decoate and *n*-undecoate. At 80°, however, the irregularity at the *n*-valerate is much less in amount and the irregularity at the *n*-decoate and the *n*-undecoate has disappeared entirely.

In ethyl alcoholic solution, there are, in addition, indications of similar irregularities at the propionate and *n*-octoate. The explanation of these results becomes clear when we consider the structural formulae for these esters (I).



It is obvious that when R contains four or nine (ten) carbon atoms, that is, in the cases of the *n*-valerate and *n*-decoate (undecoate) the "ester" chain to the right of AB will contain five and ten (eleven) carbon atoms and may be assumed to have completed just one or two turns of the spiral, respectively.

When R contains two or seven atoms, on the other hand, that is, at the propionate or *n*-octoate, the whole chain up to the asymmetric carbon atom * will contain either four carbon atoms and one oxygen atom or nine carbon atoms and one oxygen atom and may again be imagined to have completed whole turns of the spiral as before.

• It seems evident, too, that some similar cause promotes the maximum molecular rotatory power exhibited among the esters of tetrahydronaphthol (Part III, p. 1430) by the propionate (II), and also the irregular values of the rotatory powers of the esters of 1-naphthyl-*n*-hexylcarbinol (Part IX, p. 2648), particularly of the propionate and octoate in which the acyl chains vary by five carbon atoms, whilst the abnormal values (under some conditions of solution) of the acetate, $\text{CH}_3\text{C}^1\text{O}\text{O}\text{C}^2\text{H}(\text{C}^3_{10}\text{H}_7)(\text{C}^4_6\text{H}_{13})$, and of the heptoate are also noteworthy.

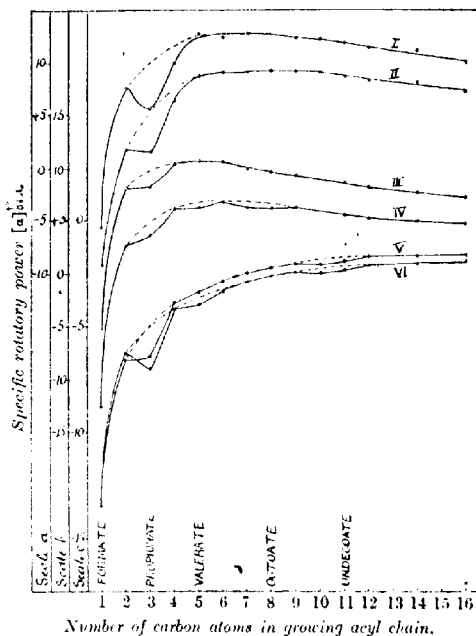
Again, the relatively high rotation of β -pentyl *n*-valerate, $\text{C}_4\text{H}_9\text{C}^4\text{O}\text{O}\text{C}^5\text{HMeC}^6_7\text{H}_{10}$ (Part V, p. 831), may be due to the ten-atomed chain—five of carbon, one of oxygen, and four other carbon atoms.

Further, among the acetates of the carbinols $\text{C}_2\text{H}_5\text{C}^1\text{H}(\text{OH})\text{C}^2_6\text{H}_{12-1}$ described in Part VII (p. 2231) the numerically high positive rotation of *d*- β -butyl acetate, $\text{CH}_3\text{C}^1\text{O}\text{O}\text{C}^2\text{HEtC}^3_3\text{H}_7$, and the abnormally high negative rotation (in carbon disulphide) of the acetate of *d*- γ -nonanol, $\text{CH}_3\text{C}^1\text{O}\text{O}\text{C}^2\text{HEtC}^3_6\text{H}_{12}$, are peculiarities which may be due to the presence in these compounds of unbranched chains of carbon and oxygen atoms numbering in all five and ten, respectively. Similar deviations from what may be called the normal rotatory power have been observed (Part VII, p. 2229) in the cases of γ -nonyl hexoate, $\text{C}_5\text{H}_{11}\text{C}^1\text{O}\text{O}\text{C}^2\text{H}(\text{C}_6\text{H}_{13})\text{C}_2\text{H}_5$, and the undecoate, $\text{C}_{10}\text{H}_{21}\text{C}^1\text{O}\text{O}\text{C}^2\text{H}(\text{C}_6\text{H}_{13})\text{C}_3\text{H}_7$, compounds which may be regarded as containing ten and fifteen atoms (one of these being oxygen), respectively, in an unbranched chain.

Other examples of this kind can be cited from the literature, and it was felt that the examination of the formic esters of the simple optically active secondary alcohols would furnish a test case of some theoretical value. When specific rotatory power is plotted against molecular weight for various series of esters, it is observed that in the case of, for example, the β -octyl esters (Part V), the γ -nonyl esters (Part VII), and the esters of benzylmethylcarbinol

(Part VIII) either the acetate or the propionate occupies an anomalous position in that it does not fit on the curve illustrating the connexion between molecular weight and rotatory power. In the case of the esters of β -butanol (Part V), on the other hand, both

FIG. 1.



The specific rotatory powers $[\alpha]_{D^{20}}$ in the homogeneous state of the normal esters of

d-Benzylmethylcarbinol at 20° (I) Scale a
 and at 120° (II) Scale a
 d- β -Cetanol at 20° (III) Scale b
 and at 120° (IV) Scale b
 and of d- γ -Nonanol at 20° (V) Scale c
 and at 120° (VI) Scale c

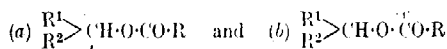
The broken curve in each case represents the apparent normal rate of increase of specific rotatory power with molecular weight.

the acetate and the propionate fall into line with the other members of the series.

It was therefore decided to make these four series of esters more complete by the inclusion of the formates. The results of the polarimetric measurements are illustrated in the figure, where they

are co-ordinated with the results obtained for the other esters of the series. They show that in each case it is the propionic member of the series rather than the acetate which shows irregularity of rotatory power, although the results of further work with optically active ethers (Parts XIV and XV, this vol., pp. 14 and 22) seem perhaps more in accordance with the idea that the acetate is the irregular member. Curve IV is particularly interesting as showing the effect of a rise in temperature in bringing to light the irregularity, latent at lower temperatures, in the rotatory power of the *n*-valerate and of the *n*-octoate of *d*-3-octanol.

It may therefore be regarded as established that in a series of normal esters of secondary alcohols exhibiting optical activity, we may expect irregularities in the rotatory power to occur at the propionate, the *n*-valerate, and *n*-octoate and the *n*-decoate or undecoate, and that these irregularities are due to the fact that the ester chain of carbon atoms assumes a spiral form with about five atoms in one complete turn, entire turns being completed at the points of irregularity. That is to say, we recognise this phenomenon in two types of chain:



In type (a) when $R = 2, 7, 12$, and in type (b) when $R = 4, 9, 14$, one or more turns of the spiral to the right of the dotted line in the formulæ are completed with consequent effect on the rotatory power.

There are several objections, of course, to this thesis. In the present state of our knowledge, it is impossible to do more than indicate possible solutions of the difficulties. First, why should the spiral be counted up to the asymmetric carbon atom *A* in type (a) above, and only to the carbonyl carbon atom *A'* in type (b)—and, further, why not include the longest possible chain in the molecule for the purpose of counting atoms? It is submitted that both the asymmetric carbon atom and the carbonyl carbon atom are singular points in the chain. They are secondary carbon atoms as distinct from the primary carbon atoms in the growing chain *R*. In view of the work of Ingold previously quoted on the variation of the intervalent angle of the carbon atom with the volume of the attached groups, and of the mathematical improbability of a spiral form being assumed by a chain of carbon atoms, it may well be that the introduction of a secondary carbon atom into a chain of primary carbon atoms already in a spiral form is sufficient to deflect the spiral, as it were, and to cause it thenceforward to assume an entirely different direction in space.

The second objection is much more serious. If it be true that

the normal form of the carbon chain is a spiral, then "straight-chain" compounds—for example, *n*-hexane, *n*-nonoic acid, *n*-dodecyl alcohol, should exist in enantiomorphous forms according as the spiral form assumed is left- or right-handed. There should be the possibility of the existence of optically active substances the plane structural formulæ of which are symmetrical. Why has this never been observed? It must be remembered that the phenomenon is more likely to be dynamic than static—the molecule cannot be assumed to be at rest in a permanently coiled-up form. Whilst it may appear far-fetched to assume that the molecule is alternately coiling up and uncoiling, and then coiling up again in the opposite sense,* it is certainly a very significant fact that the spiral differs entirely from all asymmetric forms at present known to be associated with optical activity, in that it may, whilst still remaining in space of three dimensions, be converted into its mirror image without rupture. That is to say that a right-handed spiral may be converted into a left-handed one merely by straightening it out and then coiling it up in the opposite sense—no cutting of the chain is necessary. But to convert the generally accepted asymmetric molecule into its enantiomorph a much more drastic course is necessary. Two of the groups attached to the "asymmetric" carbon atom must be removed, interchanged, and replaced in their new inverse order, thus involving more or less complete dismemberment of the molecule.

In addition to these stereochemical considerations, there are a few more or less isolated points of interest which will be touched on as briefly as possible.

d-3-Butyl Formate.—This is the simplest possible optically active ester of an organic acid. Its rotatory power is high, thus supporting the claim that complicated molecular structure is not necessary for large rotations. It will be noticed that the esters of 3-butanol do not show irregularities of rotatory power at any point in the series, at least under the experimental conditions hitherto attained.

d-3-Octyl Formate. The first levorotatory ester of *d*-3-octanol to be described, if we except *d*-3-octyl 1-naphthoate (Part XII, p. 125), which exhibits levorotation for $\lambda = 4358$ below 25° . It is not a case of inversion, for *d*-3-octanol of full dextrorotatory power is obtained by hydrolysis of the strongly levorotatory ester. Its temperature-rotation curves are similar to those of the acetate, etc., in that its levorotation increases with rise of temperature.

* It is not necessary, of course, that the coiling and uncoiling of the molecular chain should be rapid. In the liquid or dissolved state, a statistical equilibrium would be set up which, if it were disturbed, would not require a very speedy equilibration in order to avoid detection of the disturbance by the methods of resolution at present at our disposal.

whilst in the case of the acetate, etc., the dextrorotation decreases with rise of temperature, that is to say, in all cases rise of temperature produces a change in rotatory power in the same sense.

d-γ-Nonyl Formate.—Like the other aliphatic esters of *d-γ*-nonyl, the formate is levorotatory, but its rotation is numerically much greater. Its rotatory power varies scarcely at all with temperature and its temperature-rotation curves exhibit maxima (minima of levorotatory power) which move towards a higher rotation value and a lower temperature value with decreasing wave-length. In this respect it resembles *d-γ*-nonyl acetate (Part VII, p. 2242).

d-Benzylmethylcarbinyl Formate.—This ester differs from the other aliphatic esters of the same alcohol in that it is levorotatory. The temperature-rotation curves of all the esters are similar, however, just as in the case of the esters of *d-β*-octanol.

EXPERIMENTAL.

The esters were all prepared by the general method of condensing the appropriate optically active alcohol with anhydrous formic acid in the presence of zinc chloride. A considerable excess of the acid was employed in every case.

Anhydrous (98 per cent.) Formic Acid.—This was prepared by the convenient method of Maquenne (*Bull. Soc. chim.*, 1888, [ii], 50, 562). Commercial (90 per cent.) formic acid was mixed with enough pure (98 per cent.) sulphuric acid to form the monohydrate, $\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$, with all the water present. The formic acid was distilled off in a vacuum and collected in a receiver cooled in ice-water, in which it solidified (m. p. of pure formic acid = 8°). By exercising care in mixing the acids and maintaining the temperature of the mixture below 70°, both during the mixing and during the distillation, the dehydration of the formic acid to carbon monoxide was reduced to a minimum.

d-β-Butyl Formate. $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{O} \cdot \text{CO} \cdot \text{H}$.—*d-β*-Butanol (7.8 grams), formic acid (10 grams), and zinc chloride (8 grams) were heated on the water-bath for half an hour. At the end of that time, a slight odour of butylene was apparent. The reaction mixture was poured carefully into cold water, extracted with ether, and the ether extract washed repeatedly first with water, then with dilute aqueous sodium carbonate, and finally with water again. It was then dried by means of freshly ignited potassium carbonate, the ether was removed, and the ester distilled at atmospheric pressure through a fractionating column until its refractive index and rotatory power were unaltered by further distillation.

Thus prepared, *d-β*-butyl formate is a pleasant-smelling, colourless, mobile liquid, b. p. 96–97°.

d- β -Octyl Formate, $C_8H_{13}\cdot CHMe\cdot O\cdot CO\cdot H$.—This ester was prepared by heating together *d*- β -octanol (13 grams), formic acid (9 grams), and zinc chloride (5 grams) on the water-bath for two hours. At the end of that time, the reaction mixture had separated into two layers. The ester was purified as in the preceding case except that it was distilled under reduced pressure and no column was used. *d*- β -Octyl formate is a fragrant, colourless, limpid liquid, b. p. $81-82^\circ/20$ mm. On hydrolysis with aqueous caustic soda in a current of steam, it yields optically pure *d*- β -octanol.

d- γ -Nonyl Formate, $C_8H_{13}\cdot CHEt\cdot O\cdot CO\cdot H$.—The preparation of this ester followed exactly the same course as that of the β -octyl ester, using *d*- γ -nonyl alcohol (15 grams), formic acid (9 grams), and zinc chloride (7 grams). It is a colourless, limpid liquid with a pleasant odour and boils at $94.5-95^\circ/22$ mm.

d-Benzylmethylcarbinyl Formate, $C_6H_5\cdot CH_2\cdot CHMe\cdot O\cdot CO\cdot H$.—This ester was prepared by heating *d*-benzylmethylcarbinol (10 grams), formic acid (7 grams), and zinc chloride (6 grams) just as for the β -octyl and γ -nonyl formates. It is a mobile, highly refractive, colourless liquid, boiling at $108-110^\circ/19$ mm. Its odour is very penetrating but not unpleasant.

Density Determinations.

Densities were determined in a pycnometer holding about 3 c.c., except in the case of *d*- β -butyl formate, when one of about 1.5 c.c. capacity was used. The densities are calculated with reference to that of water at 4° .

d- β -Butyl formate.

t°	21.5°	45°	63°	94°
$d_4^{t^\circ}$	0.8820	0.8580	0.8364	0.8007

d- β -Octyl formate.

t°	12.5°	51°	73°	99°	134°
$d_4^{t^\circ}$	0.8718	0.8397	0.8196	0.7954	0.7591

d- γ -Nonyl formate.

t°	20°	41°	55°	84.5°	107°	130°	154°
$d_4^{t^\circ}$	0.8688	0.8509	0.8390	0.8153	0.7941	0.7778	0.7536

d-Benzylmethylcarbinyl formate.

t°	22°	42°	73°	100°	127°	152°
$d_4^{t^\circ}$	1.027	1.003	0.960	0.9572	0.9324	0.9099

Refractive Index Determinations.

Refractive indices were determined in a Pulfrich refractometer with jacketed optical parts. Water from a thermostat was pumped round the jacket to ensure temperature control to 0.1° . Monochromatic light of five wave-lengths was employed (wave-lengths

are measured in Å.U.). The molecular refractive powers of the compounds are calculated using the Lorenz-Lorentz formula, and are compared with the values obtained by using Eisenlohr's figures for the atomic refractive powers of their constituent elements.

d-β-Butyl formate.

λ	6708	5896	5790	5461	4358
$n_D^{25^\circ}$	1.3786	1.3812	1.3817	1.3828	1.3896
$[R_L]_{5896}^{25^\circ}$	observed 26.97 calculated 26.94 $\Delta = 0.03$				

d-β-Octyl formate.

$n_D^{12^\circ}$	1.4174				
$[R_L]_{5896}^{12^\circ}$	observed 45.64 calculated 45.42 $\Delta = 0.22$				

d-γ-Nonyl formate.

λ	6708	5896	5790	5461	4358
$n_D^{25^\circ}$	1.4152	1.4182	1.4178	1.4196	1.4271
$[R_L]_{5896}^{25^\circ}$	observed 50.14 calculated 50.03 $\Delta = 0.11$				

d-Benzylmethylcarbinyl formate.

λ	6708	5896	5790	5461	4358
$n_D^{25^\circ}$	1.4930	1.4975	1.4982	1.5009	1.5251
$[R_L]_{5896}^{25^\circ}$	observed 46.92 calculated 46.13 $\Delta = 0.79$				

Measurements of Rotatory Power.

The rotatory powers of the esters were measured in a 50 mm. jacketed tube round which heated mineral oil was circulated by means of a small rotary pump. The temperature of the active liquid was kept constant within 0.5° for each observation.

Table I gives the experimentally observed rotations for the 50 mm. tube. When these rotations are plotted against the corresponding temperatures, smooth curves are obtained from which the values of the rotatory power at temperature intervals of 20° were calculated. These values are collected in Table II.

TABLE I.

The observed rotatory powers of the esters in the homogeneous state.

The measurements refer to a 50 mm. tube.

d-β-Butyl formate.

α_{1932}	8.47° at 17°; 7.87° at 28°; 7.01° at 45°; 6.48° at 54°; 6.16° at 63°; 5.02° at 94°.
α_{1461}	10.12° at 17°; 9.16° at 32°; 8.45° at 45°; 7.83° at 56.5°; 7.32° at 65°; 5.96° at 94°.
α_{4358}	16.58° at 17°; 15.00° at 32°; 13.80° at 45°; 12.70° at 55.5°; 11.42° at 69°; 9.80° at 94°.

TABLE I.—(continued).

d-β-Octyl formate.

α_{5893}	— 1.72° at 16°; — 2.22° at 37°; — 2.41° at 47.5°; — 2.89° at 71°; — 3.36° at 101°; — 3.54° at 120.5°; — 3.59° at 149°.
α_{5461}	— 2.14° at 16°; — 2.62° at 38°; — 3.04° at 52°; — 3.47° at 70°; — 4.14° at 99°; — 4.38° at 126.5°; — 4.48° at 146°.
α_{4318}	— 4.11° at 16°; — 5.12° at 38.5°; — 5.54° at 49°; — 6.27° at 71°; — 7.18° at 100.5°; — 7.73° at 120°; — 7.95° at 145.5°.

d-γ-Nonyl formate.

α_{5893}	— 4.89° at 17°; — 4.80° at 50°; — 4.65° at 65°; — 4.50° at 92°; — 4.45° at 118°.
α_{5461}	— 5.83° at 17°; — 5.63° at 47°; — 5.47° at 67°; — 5.44° at 72°; — 5.27° at 93°; — 5.21° at 120°.
α_{4318}	— 10.23° at 17°; — 9.94° at 44°; — 9.69° at 70°; — 9.63° at 79°; — 9.53° at 93°; — 9.44° at 119°.

d-Benzylmethylecarbinyl formate.

α_{5893}	— 2.36° at 15°; — 2.56° at 31°; — 2.74° at 57°; — 3.05° at 89°; — 3.15° at 105°; — 3.32° at 124°.
α_{5461}	— 2.76° at 15°; — 3.04° at 30°; — 3.50° at 58°; — 3.75° at 80°; — 4.03° at 99°; — 4.23° at 113°; — 4.28° at 124°.
α_{4318}	— 5.42° at 15°; — 5.83° at 31°; — 6.01° at 42°; — 6.73° at 65°; — 6.92° at 76°; — 7.58° at 110°; — 7.96° at 125°.

TABLE II.

The specific rotatory powers of the esters in the homogeneous state.

<i>d-β-Butyl formate</i> (Mol. Wt. = 102).					<i>d-β-Octyl formate</i> (Mol. Wt. = 158).				
<i>t</i> , °	D_D^{20}	$[\alpha]_D^{20}$			<i>t</i> , °	D_D^{20}	$[\alpha]_D^{20}$		
		5893.	5461.	4358.		5893.	5461.	4358.	
20	0.8846	18.74	22.48	36.76	20	0.8658	4.16	5.04	9.93
40	0.8621	16.87	20.27	33.06	40	0.8490	5.35	6.43	12.20
60	0.8391	15.04	18.19	29.31	60	0.8313	6.45	7.84	14.29
80	0.8163	13.48	16.19	26.28	80	0.8130	7.45	9.15	16.16
					100	0.7941	8.36	10.38	18.01
					120	0.7746	9.04	11.25	19.45
					140	0.7540	9.47	11.83	20.87

<i>d-γ-Nonyl formate</i> (Mol. Wt. = 172).					<i>d-Benzylmethylecarbinyl formate</i> (Mol. Wt. = 164).				
<i>t</i> , °	D_D^{20}	$[\alpha]_D^{20}$			<i>t</i> , °	D_D^{20}	$[\alpha]_D^{20}$		
		5893.	5461.	4358.		5893.	5461.	4358.	
20	0.8688	11.28	13.47	23.48	20	0.6276	4.73	5.57	10.8
40	0.8518	11.27	13.36	23.42	40	0.6098	5.15	6.34	11.9
60	0.8349	11.26	13.24	23.42	60	0.6919	5.58	7.06	13.18
80	0.8181	11.24	13.13	23.52	80	0.9742	6.04	7.78	14.50
100	0.8011	11.25	13.11	23.72	100	0.9553	6.48	8.45	15.8
120	0.7842	11.25	13.26	24.08	120	0.9385	6.99	9.12	16.0

TABLE III.
The rotatory powers of the esters in approximately five per cent. solutions.

Ester.	Solvent.	t , °C.	Weight of ester in grams in 100 c.c. of solution.	c, obs.,		$[\alpha]_D$.
				2-dim.	4358.	
<i>d</i> . β -Butyl formate.	(Carbon disulphide)	17.5	4.53	5461.	4358.	4358.
	(Ethyl alcohol)	"	4.97	1.09	1.61	+ 11.2°
<i>d</i> . β -Octyl formate.	(Carbon disulphide)	16.5	5.82	2.25	3.80	+ 38.3
	(Ethyl alcohol)	"	6.75	2.57	4.75	+ 40.8
	(Pyridine)	"	4.67	0.99	1.70	+ 22.1
	(Acetone)	"	4.83	0.94	1.85	+ 7.3
	(Carbon disulphide)	17.5	5.48	0.70	1.13	+ 13.3
<i>d</i> . γ -Nonyl formate.	(Ethyl alcohol)	18.5	5.06	2.70	4.00	+ 22.7
	(Carbon disulphide)	17.0	5.40	1.37	1.54	+ 11.7
<i>d</i> . Benzylmethyl- carbamyl formate.	(Ethyl alcohol)	"	5.58	2.65	4.05	+ 24.6
	(Carbon disulphide)	"	5.58	0.16	0.45	+ 13.2
				0.15	0.45	+ 13.5
				0.15	0.45	+ 1.3
						+ 1.4
						+ 3.9

The rotatory powers of the esters were also measured in approximately 5 per cent. solution in carbon disulphide and in ethyl alcohol. For this purpose, approximately one gram of active substance was made up to 20 c.c. with the solvent, and the rotatory power of the solution determined in a 200 mm. tube. These results are given in Table III.

Part of the expense of this investigation was defrayed by a grant from the Government Grant Committee of the Royal Society, and, in addition, one of the authors received a personal grant from the Department of Scientific and Industrial Research.

BATTERSEA POLYTECHNIC, S.W. 11. [Received, November 1st, 1922.]

II.—*Investigations on the Dependence of Rotatory Power on Chemical Constitution. Part XIV. The Normal Aliphatic Ethers of d-β-Octanol.*

By JOSEPH KENYON and REGINALD ARTHUR McNICOL.

IN the preceding parts of this series of investigations the optical rotatory and rotatory dispersive powers of a considerable number of secondary alcohols and of esters derived from them have been examined. From the results obtained three main conclusions may be drawn.

(1) In a homologous series of optically active alcohols of the general formula $R\cdot CH(OH)\cdot R^1$, where R represents the growing aliphatic chain, departures from what may be termed the normal alteration of rotatory power with increase of molecular weight are observed when R consists of a chain of five or ten (eleven) carbon atoms.

(2) A similar phenomenon is observed in homologous series of esters of the formula $R^1R^2\cdot CH\cdot O\cdot CO\cdot R$ when the growing chain R contains five or ten (eleven) carbon atoms. It will be noticed that this case differs from (1) above in that R is not directly attached to the asymmetric carbon atom.

(3) Alcohols of simple chemical constitution possess simple rotatory dispersive powers under widely varying conditions of temperature, whereas the aliphatic esters derived from them show simple rotatory dispersive powers only at low temperatures; at higher temperatures and in solution the dispersive powers become complex.

The results obtained by observing the rotatory powers of these two classes of compound, both in the homogeneous state over a wide range of temperature and in solution at the temperature of the laboratory, make it highly probable that the differences in

dispersive power are due to some change in the molecular constitution of the esters occurring with change of conditions, and it has been suggested that this phenomenon may be due to some specific property of the carboxylic portion of the molecule.

In view of the possible effect of adjacent oxygen atoms in the carboxylic portion of the molecule, it was thought advisable to examine the rotatory powers of substances in which this possible disturbing factor is not present. To this end, a series of ethers was prepared containing in each case, as the asymmetric portion of the molecule, the *sec*.-octyl radicle, and, as the second radicle, one of the normal alkyl groups methyl, ethyl, up to *n*-nonyl. Such a series of compounds seems to fulfil the conditions laid down above. *sec*.-Octyl alcohol was chosen as the parent alcohol because it is the most readily obtainable of the optically active alcohols of simple chemical constitution.

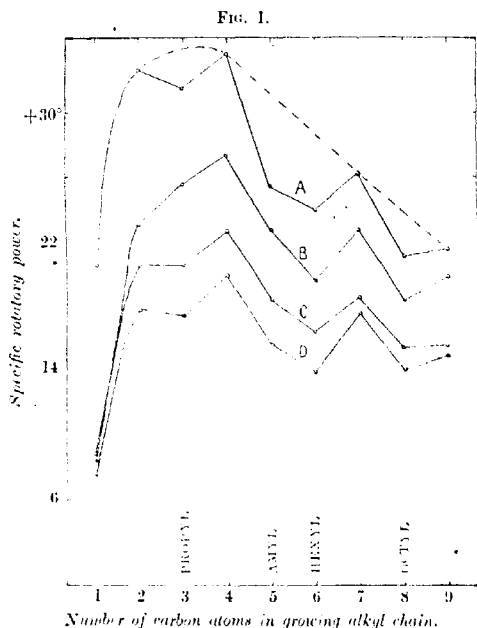
The investigation of the optical properties of these ethers has led to the following interesting results— at all temperatures between 15° and 130° they exhibit simple rotatory dispersion, for at no point within these limits does the dispersion ratio $\alpha_{4358}/\alpha_{5461}$ fall below the value 1.577, and, in addition, when the reciprocal of the rotation is plotted against the square of the wave-length of the light used, linear curves are obtained for every ether examined, showing that the one-term Drude equation expresses the relation between rotatory power and wave-length of the light used.

Determinations of the rotatory powers of the ethers in the homogeneous state over a range of temperatures 15—130° for light of different wave-lengths show the presence of marked depressions in the optical rotatory power in the case of the members containing the *n*-propyl, *n*-amyl and hexyl, and *n*-octyl radicle.

It is considered that these investigations show that the magnitude of the rotatory power may be influenced by the approximate closing of the spiral arrangement of three types of chain present in all these compounds. These are (a) any complete chain through the molecule, (b) the chain of atoms up to and including the asymmetric carbon atom, and (c) the chain of atoms attached to the asymmetric carbon atom. In the case of the secondary alcohols dealt with in the earlier parts of these investigations, conclusive evidence has been obtained that the rotatory power is affected at intervals not only by the chain of the whole molecule, but also by the chain attached to the asymmetric carbon atom, whilst in the case of the esters of these alcohols as shown in Part XIII (this vol., p. 1) the influence of chains of the types (b) and (c) is demonstrated. In the case of the ethers herein described, the evidence is not conclusive, but points to the possi-

bility that the magnitudes of the rotatory powers of different members of the series are affected by the completion of a spiral in chains of all three types.

The irregularities due to this cause may be most clearly demonstrated by plotting rotatory powers as ordinates against the number of carbon atoms in the growing chain as abscissæ. In the figure,



The ethers of α,β-Octanol.

- A. $[\alpha]_{461}^{20}$ in 5% solution in carbon disulphide.
 B. $[\alpha]_{426}^{20}$ in the homogeneous state.
 C. $[\alpha]_{461}^{20}$ " " "
 D. $[\alpha]_{461}^{20}$ in 5% solution in ethyl alcohol.

the values actually plotted are for $[\alpha]_{461}$, but strictly similar curves are obtained by plotting the specific rotatory powers for any of the wave-lengths employed.

A very unusual effect was observed when the rotations of these ethers were determined in 5 per cent. solutions in carbon disulphide and in ethyl alcohol; in all previous cases in this series of investigations, it has been found that the former solvent effects a consider-

able depressing action, and the latter solvent an exalting action, although to a less degree. In the series of ethers now being considered, however, the reverse is the case, for carbon disulphide causes enhanced rotations and ethyl alcohol depressed ones. As may be seen from the diagram, the deviations from what may be regarded as the normal values are the same in solution as for the substances in the homogeneous state.

The ethers may be prepared either according to the method of Ferns and Lapworth (T., 1912, **101**, 273), in which potassium β -octyloxide is added to a *n*-alkyl *p*-toluenesulphonate, or by allowing potassium β -octyloxide to react with a normal alkyl haloid. Samples of an ether prepared by either method are identical in rotatory power, and this fact allows of a strong presumption that no racemisation occurs during either process.

EXPERIMENTAL.

Action of Potassium on d- β -Octanol.—To, clean potassium (4 grams) covered with dry benzene (or dry ether) there was added slowly *d*- β -octanol (23 grams) at such a rate that the reaction did not become too vigorous; when most of the potassium had dissolved, the reaction was completed by gentle warming. The reaction mixture was then poured into ice-water in an atmosphere of carbon dioxide, and the whole distilled in a current of steam. The distillate was extracted with ether, the ethereal extract dried and, after removal of ether and benzene, distilled under reduced pressure. The octyl alcohol thus obtained showed $\alpha_{D, 20}^{1\%} + 19.36^\circ$ in a 2-dm. tube, whereas the original alcohol showed $\alpha_{D, 20}^{1\%} + 19.40^\circ$. Thus it is evident that no racemisation occurs under these conditions.

General Method of Preparation of the Optically Active Ethers.

To the solution (or suspension) of potassium β -octyloxide in ether (or benzene) was added the theoretical amount (calculated on the potassium used) of the alkyl bromide (or iodide), and the reaction mixture gently heated under reflux for about twenty hours, care being taken to prevent the access of moisture during this period. In the cases of methyl and ethyl iodides and ethyl bromide reacting with an ethereal solution of potassium β -octyloxide, heating is not necessary, standing at the ordinary temperature for several hours being quite sufficient. The potassium bromide (or iodide) was washed out with water, and the dried ethereal (or benzene) solution mixed with sufficient phthalic anhydride to convert unchanged *sec*-octyl alcohol into its hydrogen phthalic ester. After removing the ether (or benzene), the residue was heated at 110 – 115° for

TABLE I.

Determinations of Density (D_4^{20}) and of Rotatory Power ($\alpha_{D,0mm.}$) for the Ethers in the Homogeneous State.

*Methyl *d*-sec.-octyl ether.*

D_4^{20}	0.8076 at 19°; 0.7870 at 43.4°; 0.7700 at 62°; 0.7536 at 81.4°; 0.7391 at 99.4°.
α_{4438}	2.67° at 14°; 2.07° at 53°; 1.85° at 61°; 1.55° at 81.5°; 1.36° at 101°.
α_{5461}	3.57° at 14°; 2.70° at 51.4°; 2.67° at 61°; 2.33° at 82°; 1.86° at 104°.
α_{5066}	4.29° at 14°; 3.24° at 53.5°; 3.16° at 61°; 2.65° at 81.5°; 2.43° at 98°.
α_{1800}	4.81° at 14°; 3.56° at 54°; 3.54° at 61°; 3.09° at 81°; 2.83° at 98°.
α_{1478}	5.06° at 14°; 3.75° at 55°; 3.70° at 61°; 3.22° at 81.5°; 3.00° at 98°.
α_{1328}	5.87° at 14°; 4.60° at 51°; 4.18° at 61°; 3.76° at 82°; 3.22° at 98°.

*Ethyl *d*-sec.-octyl ether.*

D_4^{20}	0.7895 at 17.2°; 0.7719 at 39.7°; 0.7545 at 58.5°; 0.7387 at 79.0°; 0.7202 at 100.5°.
α_{4438}	5.86° at 17.8°; 4.94° at 56°; 4.53° at 81°; 4.15° at 96°; 3.89° at 113°.
α_{5461}	8.08° at 17.8°; 6.97° at 54°; 6.24° at 79°; 5.68° at 97°; 5.47° at 110°.
α_{5066}	9.61° at 17.8°; 8.04° at 56°; 7.30° at 81°; 6.69° at 97°; 6.31° at 112°.
α_{1800}	10.47° at 17.8°; 9.10° at 55.5°; 8.29° at 80°; 7.56° at 95°; 7.12° at 112°.
α_{1478}	11.31° at 17.8°; 9.65° at 55°; 8.69° at 79°; 7.99° at 95°; 7.50° at 110°.
α_{1328}	13.09° at 17.8°; 11.19° at 54°; 10.04° at 79°; 9.19° at 95°; 8.81° at 105°.

n-Propyl *d*-sec.-octyl ether.

D_4^{20}	0.7971 at 12°; 0.7598 at 61°; 0.7435 at 80°; 0.7303 at 96°.
α_{5461}	8.30° at 16.5°; 7.27° at 50.5°; 6.76° at 67°; 6.10° at 97°; 5.61° at 121°.
α_{1328}	13.42° at 16.5°; 11.70° at 50.5°; 10.97° at 67°; 9.77° at 96°; 9.12° at 120°.

n-Butyl *d*-sec.-octyl ether.

D_4^{20}	0.7971 at 18.5°; 0.7766 at 45°; 0.7568 at 70°; 0.7226 at 103°; 0.7063 at 135°.
α_{4438}	6.62° at 20°; 5.64° at 56°; 5.24° at 74°; 4.75° at 102°; 4.47° at 119°.
α_{5461}	8.94° at 20°; 7.75° at 57°; 7.18° at 76°; 6.70° at 98°; 6.05° at 118°.
α_{5186}	10.41° at 20°; 8.88° at 59°; 8.41° at 75°; 7.66° at 101°; 7.10° at 119°.
α_{1470}	11.82° at 20°; 9.98° at 59°; 9.20° at 75°; 8.59° at 101°; 7.89° at 119°.
α_{1478}	12.34° at 20°; 10.60° at 58°; 9.80° at 76°; 9.21° at 99°; 8.38° at 119°.
α_{1328}	14.38° at 20°; 12.16° at 57°; 11.37° at 76°; 10.62° at 98°; 9.69° at 118°.

n-Amyl *d*-sec.-octyl ether.

D_4^{20}	0.7989 at 20°; 0.7820 at 42.5°; 0.7696 at 60°; 0.7484 at 84.4°; 0.7233 at 114.8°; 0.7023 at 139.6°.
α_{4438}	5.25° at 17°; 4.91° at 35°; 4.61° at 53°; 4.18° at 76°; 4.00° at 101°; 3.50° at 135°.
α_{5461}	7.36° at 17°; 6.94° at 35°; 6.34° at 54°; 5.90° at 72°; 5.41° at 105°; 4.97° at 135°.
α_{5066}	8.47° at 17°; 8.19° at 32°; 7.51° at 63°; 6.92° at 77.5°; 6.44° at 100°; 5.73° at 129°.
α_{1800}	9.63° at 17°; 9.17° at 31°; 8.57° at 54°; 7.84° at 77.5°; 7.33° at 100°; 6.58° at 130°.
α_{1478}	10.23° at 17°; 9.62° at 30°; 8.92° at 56°; 8.19° at 76°; 7.64° at 100°; 6.93° at 131°.
α_{1328}	11.79° at 17°; 11.08° at 35°; 10.33° at 54°; 9.50° at 74°; 8.75° at 102°; 7.85° at 133°.

TABLE I.—(continued).

n-Hexyl *d*-sec.-octyl ether.
$$D_D^{25} \text{ 0.8047 at } 17.0^\circ; \text{ 0.7881 at } 40.4^\circ; \text{ 0.7723 at } 62.0^\circ; \text{ 0.7568 at } 82.5^\circ; \text{ 0.7149 at } 137^\circ.$$

$$\alpha_{4358} \text{ 4.66}^\circ \text{ at } 21.2^\circ; \text{ 4.29}^\circ \text{ at } 42^\circ; \text{ 3.77}^\circ \text{ at } 80^\circ; \text{ 3.39}^\circ \text{ at } 108^\circ; \text{ 2.98}^\circ \text{ at } 137^\circ.$$

$$\alpha_{5461} \text{ 6.52}^\circ \text{ at } 21.2^\circ; \text{ 6.02}^\circ \text{ at } 41^\circ; \text{ 5.41}^\circ \text{ at } 78^\circ; \text{ 4.77}^\circ \text{ at } 109^\circ; \text{ 4.17}^\circ \text{ at } 138^\circ.$$

$$\alpha_{5286} \text{ 7.48}^\circ \text{ at } 21.2^\circ; \text{ 6.96}^\circ \text{ at } 42^\circ; \text{ 6.17}^\circ \text{ at } 80^\circ; \text{ 5.59}^\circ \text{ at } 106^\circ; \text{ 4.88}^\circ \text{ at } 137^\circ.$$

$$\alpha_{4300} \text{ 8.45}^\circ \text{ at } 21.2^\circ; \text{ 7.87}^\circ \text{ at } 42^\circ; \text{ 6.92}^\circ \text{ at } 80^\circ; \text{ 6.26}^\circ \text{ at } 107^\circ; \text{ 5.60}^\circ \text{ at } 136^\circ.$$

$$\alpha_{4478} \text{ 8.89}^\circ \text{ at } 21.2^\circ; \text{ 8.33}^\circ \text{ at } 42^\circ; \text{ 7.26}^\circ \text{ at } 79^\circ; \text{ 6.46}^\circ \text{ at } 108^\circ; \text{ 5.87}^\circ \text{ at } 135^\circ.$$

$$\alpha_{4368} \text{ 10.37}^\circ \text{ at } 21.2^\circ; \text{ 9.67}^\circ \text{ at } 42^\circ; \text{ 8.34}^\circ \text{ at } 78^\circ; \text{ 7.51}^\circ \text{ at } 108^\circ; \text{ 6.56}^\circ \text{ at } 138^\circ.$$
n-Heptyl *d*-sec.-octyl ether.
$$D_D^{25} \text{ 0.8034 at } 22^\circ; \text{ 0.7776 at } 59^\circ; \text{ 0.7672 at } 73^\circ; \text{ 0.7440 at } 101^\circ; \text{ 0.7290 at } 125^\circ.$$

$$\alpha_{4358} \text{ 5.38}^\circ \text{ at } 16^\circ; \text{ 4.81}^\circ \text{ at } 42^\circ; \text{ 4.42}^\circ \text{ at } 64^\circ; \text{ 4.20}^\circ \text{ at } 85^\circ; \text{ 3.88}^\circ \text{ at } 117^\circ.$$

$$\alpha_{5461} \text{ 7.50}^\circ \text{ at } 16^\circ; \text{ 6.81}^\circ \text{ at } 43^\circ; \text{ 6.47}^\circ \text{ at } 61^\circ; \text{ 5.99}^\circ \text{ at } 85^\circ; \text{ 5.49}^\circ \text{ at } 121^\circ.$$

$$\alpha_{5286} \text{ 8.81}^\circ \text{ at } 16^\circ; \text{ 8.02}^\circ \text{ at } 42^\circ; \text{ 7.29}^\circ \text{ at } 66^\circ; \text{ 6.80}^\circ \text{ at } 85^\circ; \text{ 6.18}^\circ \text{ at } 118^\circ.$$

$$\alpha_{4300} \text{ 9.81}^\circ \text{ at } 16^\circ; \text{ 9.09}^\circ \text{ at } 43^\circ; \text{ 8.38}^\circ \text{ at } 63^\circ; \text{ 7.90}^\circ \text{ at } 83^\circ; \text{ 7.09}^\circ \text{ at } 118^\circ.$$

$$\alpha_{4478} \text{ 10.49}^\circ \text{ at } 16^\circ; \text{ 9.48}^\circ \text{ at } 41^\circ; \text{ 8.89}^\circ \text{ at } 64^\circ; \text{ 8.49}^\circ \text{ at } 80^\circ; \text{ 7.23}^\circ \text{ at } 119^\circ.$$

$$\alpha_{4358} \text{ 12.09}^\circ \text{ at } 16^\circ; \text{ 10.87}^\circ \text{ at } 45^\circ; \text{ 10.18}^\circ \text{ at } 64^\circ; \text{ 9.50}^\circ \text{ at } 82^\circ; \text{ 8.41}^\circ \text{ at } 120^\circ.$$
n-Octyl *d*-sec.-octyl ether.
$$D_D^{25} \text{ 0.8099 at } 15^\circ; \text{ 0.7929 at } 43^\circ; \text{ 0.7780 at } 65^\circ; \text{ 0.7459 at } 109^\circ; \text{ 0.7254 at } 143^\circ.$$

$$\alpha_{4358} \text{ 4.36}^\circ \text{ at } 20^\circ; \text{ 4.61}^\circ \text{ at } 42^\circ; \text{ 3.75}^\circ \text{ at } 60^\circ; \text{ 3.07}^\circ \text{ at } 108^\circ; \text{ 2.87}^\circ \text{ at } 130^\circ.$$

$$\alpha_{5461} \text{ 6.20}^\circ \text{ at } 20^\circ; \text{ 5.59}^\circ \text{ at } 43^\circ; \text{ 5.16}^\circ \text{ at } 61^\circ; \text{ 4.35}^\circ \text{ at } 108^\circ; \text{ 4.22}^\circ \text{ at } 130^\circ.$$

$$\alpha_{5286} \text{ 7.10}^\circ \text{ at } 20^\circ; \text{ 6.51}^\circ \text{ at } 42^\circ; \text{ 6.01}^\circ \text{ at } 61^\circ; \text{ 5.00}^\circ \text{ at } 108^\circ; \text{ 4.79}^\circ \text{ at } 130^\circ.$$

$$\alpha_{4300} \text{ 8.05}^\circ \text{ at } 20^\circ; \text{ 7.35}^\circ \text{ at } 42^\circ; \text{ 6.68}^\circ \text{ at } 62^\circ; \text{ 5.54}^\circ \text{ at } 108^\circ; \text{ 5.37}^\circ \text{ at } 130^\circ.$$

$$\alpha_{4478} \text{ 8.39}^\circ \text{ at } 20^\circ; \text{ 7.58}^\circ \text{ at } 43^\circ; \text{ 6.97}^\circ \text{ at } 62^\circ; \text{ 5.81}^\circ \text{ at } 109^\circ; \text{ 5.57}^\circ \text{ at } 130^\circ.$$

$$\alpha_{4358} \text{ 9.98}^\circ \text{ at } 20^\circ; \text{ 8.92}^\circ \text{ at } 44^\circ; \text{ 8.36}^\circ \text{ at } 62^\circ; \text{ 6.80}^\circ \text{ at } 105^\circ; \text{ 6.59}^\circ \text{ at } 125^\circ.$$
n-Nonyl *d*-sec.-octyl ether.
$$D_D^{25} \text{ 0.8110 at } 17^\circ; \text{ 0.7911 at } 47^\circ; \text{ 0.7747 at } 66^\circ; \text{ 0.7573 at } 89^\circ; \text{ 0.7409 at } 116^\circ.$$

$$\alpha_{4358} \text{ 4.49}^\circ \text{ at } 20^\circ; \text{ 4.17}^\circ \text{ at } 45^\circ; \text{ 3.72}^\circ \text{ at } 75^\circ; \text{ 3.48}^\circ \text{ at } 97^\circ; \text{ 3.30}^\circ \text{ at } 116^\circ.$$

$$\alpha_{5461} \text{ 6.13}^\circ \text{ at } 20^\circ; \text{ 5.77}^\circ \text{ at } 44^\circ; \text{ 5.19}^\circ \text{ at } 75^\circ; \text{ 4.86}^\circ \text{ at } 95^\circ; \text{ 4.54}^\circ \text{ at } 118^\circ.$$

$$\alpha_{5286} \text{ 7.27}^\circ \text{ at } 20^\circ; \text{ 6.62}^\circ \text{ at } 46^\circ; \text{ 6.10}^\circ \text{ at } 75^\circ; \text{ 5.66}^\circ \text{ at } 96^\circ; \text{ 5.39}^\circ \text{ at } 117^\circ.$$

$$\alpha_{4300} \text{ 8.18}^\circ \text{ at } 20^\circ; \text{ 7.50}^\circ \text{ at } 46^\circ; \text{ 6.74}^\circ \text{ at } 75^\circ; \text{ 6.29}^\circ \text{ at } 95^\circ; \text{ 5.93}^\circ \text{ at } 117^\circ.$$

$$\alpha_{4478} \text{ 8.63}^\circ \text{ at } 20^\circ; \text{ 8.96}^\circ \text{ at } 45^\circ; \text{ 7.95}^\circ \text{ at } 76^\circ; \text{ 6.71}^\circ \text{ at } 93^\circ; \text{ 6.21}^\circ \text{ at } 115^\circ.$$

$$\alpha_{4358} \text{ 9.97}^\circ \text{ at } 20^\circ; \text{ 9.19}^\circ \text{ at } 44^\circ; \text{ 8.27}^\circ \text{ at } 76^\circ; \text{ 7.86}^\circ \text{ at } 92.5^\circ; \text{ 7.37}^\circ \text{ at } 115^\circ.$$

ten hours. The cold reaction product was dissolved in ether, extracted with dilute sodium carbonate solution, dried, the ether evaporated, and the resulting *d*-3-octyl alkyl ether purified by distillation under reduced pressure. In no case was any evidence obtained of the presence of unsaturated compounds. The sodium carbonate washings, after acidification, gave *d*-3-octyl hydrogen phthalate of the usual rotatory power.

Preparation of Ethyl d-sec.-Octyl Ether by the Use of Ethyl *p*-Toluene-sulphonate.

The procedure described by Ferns and Lapworth (*loc. cit.*) was closely followed. Potassium *d*-3-octyloxide in benzene solution was allowed to react with the calculated amount of ethyl *p*-toluene-

TABLE II.
Physical Properties of Ethers of d-β-Octanol.

Molecular refractive power.

Ether.	B. p. (C. mm.)	d_4^{20} .	n_D^{20} .	Found.	Diff. from calc. value.	n_D^{20} .	n_D^{20} .	Refractive dispersive power.
Methyl	70–77° 44	0.8094	1.4212	4.5–27	– 0.13	1.4232	1.4317	0.02709
Ethyl	63–65° 14	0.7861	1.4136	50–11	– 0.07	1.4119	1.4233	0.02721
n-Propyl	76 18	0.7887	1.4148	54–59	– 0.05	—	1.4173	—
n-Butyl	85–86° 14	0.7923	1.4168	59–32	– 0.07	1.4146	1.4255	0.02614
n-Amyl	99 15	0.7958	1.4218	63–84	– 0.03	1.4199	1.4309	0.02598
n-Hexyl	115 15	0.7983	1.4252	68–65	– 0.13	1.4232	1.4345	0.02644
n-Heptyl	129 18	0.8017	1.4267	72–98	– 0.13	1.4244	1.4280	0.02653
n-Octyl	146 13	0.8038	1.4301	77–87	– 0.11	1.4283	1.4319	0.02643
n-Nonyl	163 18	0.8042	1.4325	82–61	– 0.16	1.4307	1.4344	0.02654

TABLE III.

Comparison of Specific Rotatory Powers at 20° and 120°.

Ether.	$[\alpha]_D^{20}$.	$[\alpha]_D^{120}$.
Methyl	6438	4678
Ethyl	6438	4678
n-Propyl	6438	4678
n-Butyl	6438	4678
n-Amyl	6438	4678
n-Hexyl	6438	4678
n-Heptyl	6438	4678
n-Octyl	6438	4678
n-Nonyl	6438	4678

TABLE IV.
Comparison of Specific Rotatory Powers in 5 per cent. Solution.

(1) In carbon disulphide solution at room temperature in a 20-cm. tube.

	Grams in 100 c.c.	Observed rotation.									
		6438.	5461.	5086.	4800.	4678.	4358.	6438.	5461.	5086.	4800.
Ethyl	4.97	1.52	2.03	2.42	2.70	2.83	3.57	12.31	32.68	24.31	28.10
Methyl	4.72	2.34	3.15	3.91	4.42	4.62	5.62	24.27	61.42	45.50	58.16
Ethyl	5.47	3.44	3.44	3.91	4.42	4.62	5.62	24.27	61.42	45.50	58.16
n-Propyl	3.56	2.10	3.08	3.64	4.18	4.44	5.27	24.58	53.79	39.00	45.86
n-Butyl	3.33	1.31	1.78	2.16	2.41	2.59	3.09	19.00	25.24	30.62	33.16
n-Amyl	3.17	1.14	1.52	1.87	2.11	2.22	2.59	17.97	23.96	28.51	30.61
n-Hexyl	3.26	1.63	2.25	2.80	3.21	3.37	3.85	19.15	26.20	32.48	34.71
n-Heptyl	3.41	1.10	1.43	1.77	1.90	2.05	2.42	16.14	20.60	25.08	26.20
n-Octyl	3.30	1.42	1.42	1.77	1.90	2.05	2.42	16.14	20.60	25.08	26.20
n-Nonyl	3.30	1.42	1.42	1.77	1.90	2.05	2.42	16.14	20.60	25.08	26.20

(2) In absolute ethyl alcohol solution at room temperature in a 20-cm. tube.

	Grams in 20 c.c.	Observed rotation.									
		6438.	5461.	5086.	4800.	4678.	4358.	6438.	5461.	5086.	4800.
Ethyl	3.92	0.50	0.59	0.70	0.73	0.79	0.96	0.37	1.52	8.92	10.07
Methyl	4.95	1.38	1.75	2.20	2.51	2.63	2.97	13.94	17.28	22.22	25.35
Ethyl	5.10	1.76	1.76	2.18	2.44	2.54	2.96	15.67	16.84	24.06	26.93
n-Propyl	4.53	1.19	1.49	1.81	2.03	2.10	2.43	12.51	15.56	18.82	21.12
n-Butyl	4.81	1.31	1.47	1.81	2.03	2.10	2.43	12.51	15.56	18.82	21.12
n-Amyl	3.52	0.91	1.07	1.31	1.41	1.54	1.70	13.32	17.66	20.96	23.13
n-Hexyl	4.84	1.28	1.71	2.03	2.24	2.42	2.76	13.32	17.66	20.96	23.13
n-Heptyl	2.93	0.60	0.81	0.92	1.04	1.08	1.30	14.02	15.73	17.78	18.46
n-Octyl	4.21	1.26	1.26	1.59	1.59	1.59	1.59	14.97	14.97	15.73	17.78
n-Nonyl	4.21	1.26	1.26	1.59	1.59	1.59	1.59	14.97	14.97	15.73	17.78

sulphonate dissolved in benzene. The gelatinous precipitate which had formed during six hours' heating on the water-bath was removed by filtration, and the filtrate warmed with aqueous alkali, washed with water, dried, and fractionally distilled under diminished pressure. In this way there were obtained, by the use of 8 grams of potassium, 5.4 grams of ethyl *d*-sec.-octyl ether with a b. p. $65^{\circ}/16$ mm. and $n_{D}^{20} + 8.03^{\circ}$ for 100 mm. These figures are in very close agreement with those given by the ether prepared by the general method described above using either ethyl bromide or ethyl iodide.

All the ethers, which were obtained, in yields of 50–60 per cent. of the theoretical, are colourless, mobile liquids. The lower members possess somewhat penetrating but not unpleasant odours; some of their physical constants are collected in Table II.

Measurements of the rotations of these substances in ethyl alcohol and carbon disulphide solution were made at room temperature and at approximately 5 per cent. concentration.

The authors desire to thank Mr. H. Hunter for valuable assistance, and the Government Grant Committee of the Royal Society for a grant with which most of the material used has been purchased.

BATTERSEA POLYTECHNIC, S.W. 11.

[Received, November 1st, 1922.]

III.—*Investigations on the Dependence of Rotatory Power on Chemical Constitution. Part XV. Some n-Alkyl Ethers of d-Benzylmethylcarbinol.*

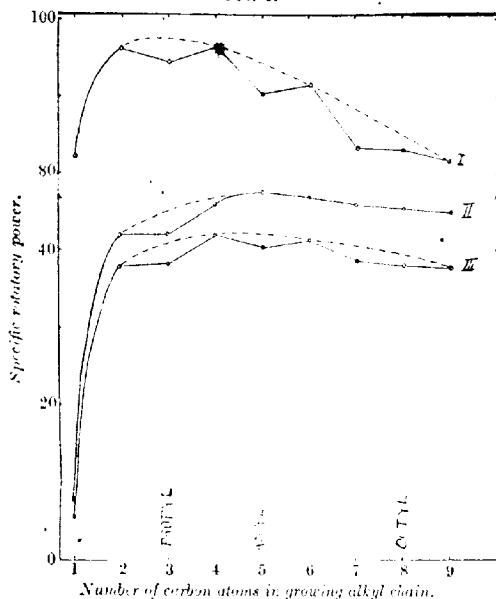
By HENRY PHILLIPS.

OF the optically active compounds which exhibit complex rotatory dispersion, the great majority contain the carboxyl group (or its equivalents, the carboalkyloxy or the xanthogenic ester group) and therefore it has been suggested that complex rotatory dispersion may be a general property of the carboxyl group and may even be specifically due to the variable valency of the oxygen atoms contained in it.

It is accordingly of interest to examine other optically active compounds containing an oxygen atom in the molecule in order to test this point. In the earlier parts of these investigations it has been shown that most secondary alcohols under very varied conditions of temperature exhibit simple rotatory dispersion, whilst in Part XIV (this vol., p. 14) there is described a homologous series of nine optically active ethers, all of which show simple rotatory dispersion. An extension of the latter investigation appeared

desirable and accordingly a series of normal alkyl ethers of *d*-benzylmethylecarbinol was prepared and examined, with results which are discussed and detailed in this paper. *d*-Benzylmethylecarbinol was chosen for this purpose because its rotatory power is high and only slightly influenced by temperature. It can also be obtained fairly readily in a state of optical purity (Part VI, T., 1914, 106, 1115).

FIG. 1.



The Ethers of *d*-Benzylmethylecarbinol.

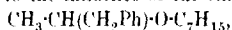
- I. $[\alpha]_{D}^{25}$ in 5% solution in carbon disulphide.
- II. $[\alpha]_{D}^{25}$ " " " " " ethyl alcohol.
- III. $[\alpha]_{D}^{25}$ in the homogeneous state.

Nine members of the series $C_6H_5 \cdot CH_2 \cdot CH(CH_3) \cdot OR$, where R represents a normal alkyl group, have been prepared by the method described in Part XIV (*loc. cit.*) and shown to exhibit simple rotatory dispersion over the temperature range 20–140°.

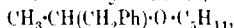
Further support is thus afforded to the view that complex rotatory dispersion must be regarded as a property of the carboxyl group as a whole and not of any one atom in it. That is to say, it is to the propinquity of the oxygen atoms in this group that the equi-

librium $\text{—C} \begin{smallmatrix} \text{O} \\ \diagup \\ \text{OH} \end{smallmatrix} \rightleftharpoons \text{—C} \begin{smallmatrix} \text{O} \\ \diagdown \\ \text{OH} \end{smallmatrix}$, with consequent complexity of rotatory dispersion, is probably due. In alcohols, $\text{R} \cdot \text{OH}$, and ethers, $\text{R}' \cdot \text{O} \cdot \text{R}''$, it may be concluded that oxygen atoms in different molecules are not able to approach sufficiently near to each other to employ their subsidiary valencies, with the result that there is only one kind of molecule present in the substance, which therefore shows simple rotatory dispersion. This is well borne out by the fact that ethers and alcohols are known to associate only slightly if at all.

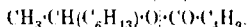
The magnitudes of the rotatory powers of the members of this series of ethers, as will be seen from Fig. 1, show remarkable irregularities. Assuming that the normal alteration of specific rotatory power with the growth of the alkyl chain is correctly indicated in the figure, it will be seen that depressions in the rotatory power occur at the propyl, amyl, heptyl, and octyl members. By analogy with previous results, the depressions at the propyl and octyl members are ascribed to the influence of the chain of five or ten atoms up to and including the asymmetric carbon atom, that at the heptyl member to the influence of the chain



whilst the depression at the amyl member,



is analogous to similar alteration in rotatory power exhibited by the valerates in some series of esters, as, for example,



EXPERIMENTAL.

Preparation of d-Benzylmethylcarbinol.—The optically active alcohol required for this research was prepared by the method given in Part VI. One thousand six hundred and seventy grams of benzyl methyl ketone were obtained by the passage of 2660 grams of phenylacetic acid, dissolved in 11,450 grams of glacial acetic acid, through a silica tube heated at 400° and half filled with thoria. The ketone was reduced in boiling ethyl alcoholic solution by means of sodium to the corresponding alcohol, which was converted into the hydrogen phthalic ester. One thousand nine hundred grams of this ester were obtained, fractional crystallisation of the brucine salt of which from acetone yielded the pure *l*BdA salt. From this pure salt 230 grams of pure *d*-benzylmethylcarbinol were obtained, $d_{20}^{25} = 0.9877$; $n_{\text{D}}^{20} = 1.5194$; $\alpha_{\text{D}}^{20} + 32.76^\circ$; $\alpha_{\text{Na}}^{20} + 33.22^\circ$; $\alpha_{\text{Na}}^{25} + 33.28^\circ$.

The yield of *l*BdA salt was diminished in the resolution by the crystallisation from the concentrated mother-liquors of the corre-

TABLE I.
n-Alkyl Ethers of *n*-Benzylmethylcarbinol.

	Boiling point, ° mm.	λ	λ	λ	λ	n_D^{20}	λ	λ	λ	Observed $\lambda = 5896$, 46.67	Diff. from calc., + 0.25
	85.12	6438	5896	5461	5086	4800	4678	4598	1.5082	1.5082	+ 0.25
Methyl	93.19	14875	14909	14942	14978	15015	15031	15047	1.5047	1.5047	+ 0.49
Ethyl	103.13	14842	14875	14906	14942	14976	14994	14987	1.4987	1.4987	+ 0.15
Propyl	115.12	14787	14818	14849	14874	14916	14933	14949	1.4949	1.4949	+ 0.34
Butyl	127.14	14761	14791	14819	14854	14884	14900	14913	1.4913	1.4913	+ 0.46
Amyl	137.14	14756	14783	14783	14783	14807	14837	14851	1.4895	1.4895	+ 0.56
Hexyl	156.19	14722	14750	14778	14778	14807	14837	14851	1.4892	1.4892	+ 0.50
Heptyl	170.12	14720	14748	14775	14775	14804	14832	14847	1.4889	1.4889	+ 0.30
Octyl	188.20	14717	14747	14773	14773	14773	14773	14773	1.4889	1.4889	+ 0.30

sponding IBA salt. Complicated mixtures of the two salts were obtained on recrystallisation, which, however, finally resulted in the isolation of a small quantity of almost pure IBA salt. From this were isolated 6 grams of *l*-benzylmethylecarbinol, $\alpha_{D}^{20} = -30.90^\circ$.

Action of Potassium on Benzylmethylecarbinol.—Fifteen grams of a partly active alcohol, with $\alpha_{D}^{20} = -6.13^\circ$ in a 50 mm. tube, dissolved in 100 c.c. of dried benzene, were treated with 2 grams of powdered potassium. On complete dissolution of the metal, the *l*-alcohol was recovered. It had $\alpha_{D}^{20} = -6.09^\circ$ in a 50 mm. tube.

General Method of Preparation of the Active Ethers.—Except for the use of 3 grams of potassium with 11 grams of the *d*-alcohol, dissolved in benzene, the method employed was the same as that given in Part XIV (*loc. cit.*). The yield was 30—40 per cent. of the theoretical.

The lower members of the series are pleasant-smelling liquids; the methyl and ethyl ethers have odours reminiscent of nerol.

In Table I are given some physical properties of the ethers, whilst in Table III are recorded the specific rotatory powers calculated from the observed rotatory powers given in Table II. The determinations of rotatory power in ethyl alcohol and in carbon disulphide are tabulated in Tables IV and V, respectively.

The densities were determined in a pycnometer holding about 3 c.c. The rotations were measured in 50 mm. tubes, round which heated mineral oil was circulated by means of a pump, but are here given as for 100 mm.

TABLE II.

Observations of Density (D_4^{20}) and Rotatory Power (α_{100}^{20}) in the Homogeneous State of the n-Alkyl Ethers of d-Benzylmethylecarbinol.

Methyl.

Density	0.9273 at 27°; 0.9135 at 47.5°; 0.8909 at 74.5°; 0.8718 at 96.3°; 0.8530 at 112°; 0.8392 at 131.5°.
α_{D}^{20}	4.34° at 18°; 4.20° at 29.5°; 3.68° at 47.5°; 3.24° at 67°; 2.64° at 88°; 2.04° at 109°.
α_{D}^{20}	6.00° at 18°; 5.10° at 36.4°; 4.76° at 47°; 4.18° at 62°; 3.50° at 83°; 2.80° at 106°.
α_{D}^{20}	7.32° at 18°; 6.68° at 28°; 5.88° at 47.5°; 4.92° at 65°; 3.88° at 88°; 3.16° at 108°.
α_{D}^{20}	8.34° at 18°; 7.92° at 27°; 6.82° at 47.5°; 5.80° at 63°; 4.62° at 88°; 3.66° at 107°.
α_{D}^{20}	8.80° at 18°; 8.28° at 26°; 7.20° at 47.5°; 6.28° at 62.5°; 4.94° at 87°; 4.00° at 106°.
α_{D}^{20}	10.22° at 18°; 9.04° at 34°; 6.96° at 61°; 6.26° at 70°; 5.52° at 83.5°; 4.38° at 102°; 4.50° at 106°.

Wide cooling.

TABLE II.—(continued).

Ethyl.

Density 0.9171 at 24°; 0.9068 at 36.5°; 0.8781 at 71.5°; 0.8370 at 101.5°; 0.8344 at 123°; 0.8145 at 144.5°.

$\alpha_{443.8}$ 16.18° at 22°; 15.46° at 43°; 14.22° at 67°; 13.30° at 87.2°; 12.10° at 111° *; 11.42° at 133°.

$\alpha_{546.1}$ 23.80° at 19°; 20.48° at 67°; 18.98° at 87°; 17.72° at 112°; 16.84° at 121°; 15.00° at 140°.

$\alpha_{568.8}$ 27.60° at 22°; 26.20° at 43°; 24.44° at 67°; 22.64° at 87°; 21.10° at 111° *; 19.88° at 133°.

α_{1800} 32.02° at 22°; 30.46° at 43°; 28.40° at 67°; 26.52° at 87°; 24.30° at 113° *; 22.80° at 133°.

$\alpha_{667.8}$ 34.38° at 22°; 32.28° at 43°; 30.42° at 67°; 28.22° at 87°; 26.16° at 113° *; 24.70° at 133°.

$\alpha_{335.8}$ 41.00° at 19°; 38.14° at 44°; 35.92° at 67°; 32.92° at 87°; 30.58° at 112°; 28.24° at 131°.

n-Propyl.

Density 0.9058 at 28°; 0.8871 at 53°; 0.8662 at 78°; 0.8486 at 99°; 0.8342 at 114°; 0.8312 at 120°.

$\alpha_{443.8}$ 16.10° at 23°; 15.34° at 45°; 14.62° at 60°; 14.42° at 70° *; 13.96° at 81°; 13.26° at 95.5°; 12.66° at 111°.

$\alpha_{546.1}$ 23.52° at 22°; 22.16° at 45°; 20.86° at 62°; 20.22° at 72° *; 19.72° at 81°; 18.86° at 94°; 17.98° at 111°.

$\alpha_{568.8}$ 27.74° at 23°; 26.32° at 45°; 24.98° at 60.5°; 24.26° at 70.4° *; 23.38° at 81°; 22.36° at 95°; 21.62° at 110.5°.

α_{1800} 31.78° at 23°; 30.06° at 45°; 28.42° at 61°; 27.72° at 71° *; 26.86° at 81°; 25.66° at 95°; 24.68° at 111°.

$\alpha_{667.8}$ 33.80° at 23°; 32.00° at 45°; 29.98° at 62°; 28.34° at 80°; 27.04° at 94.5°; 26.16° at 110°.

$\alpha_{335.8}$ 40.50° at 23°; 37.76° at 45°; 36.08° at 61.5°; 34.70° at 72° *; 33.88° at 81°; 32.54° at 94°; 30.98° at 110.5°.

n-Butyl.

Density 0.8973 at 27°; 0.8857 at 43°; 0.8686 at 65°; 0.8528 at 84°; 0.8308 at 112°.

$\alpha_{443.8}$ 17.46° at 21°; 16.78° at 45°; 16.02° at 60.5°; 15.52° at 77°; 14.64° at 94°; 14.32° at 104.5° *; 13.66° at 121°.

$\alpha_{546.1}$ 24.94° at 21.5°; 23.96° at 43°; 22.40° at 63°; 21.68° at 75.5°; 20.20° at 98°; 19.88° at 105.5°; 19.26° at 118°.

$\alpha_{568.8}$ 34.18° at 21°; 32.40° at 45°; 30.54° at 61.5°; 29.54° at 77°; 28.04° at 96°; 27.28° at 105°; 26.30° at 120°.

α_{1800} 29.76° at 21°; 28.24° at 45°; 26.74° at 61°; 25.72° at 77°; 24.46° at 94.5°; 23.82° at 104.5° *; 22.96° at 120°.

$\alpha_{667.8}$ 35.86° at 21°; 34.10° at 44°; 32.32° at 62°; 31.14° at 77°; 29.44° at 96.5°; 28.62° at 105° *; 27.76° at 119°.

$\alpha_{335.8}$ 43.36° at 22°; 38.54° at 62°; 37.08° at 75°; 35.98° at 84° *; 34.94° at 97.5°; 34.00° at 106°; 33.00° at 120°.

n-Amyl.

Density 0.8871 at 29°; 0.8777 at 42°; 0.8484 at 80°; 0.8301 at 102°; 0.8153 at 122°; 0.7994 at 141°.

$\alpha_{546.1}$ 20.26° at 22°; 19.12° at 41°; 18.62° at 58°; 17.98° at 74°; 16.84° at 90°; 15.74° at 110°; 15.16° at 120°.

$\alpha_{568.8}$ 24.00° at 20.5°; 22.72° at 41°; 21.98° at 57°; 21.32° at 73°; 19.88° at 93°; 19.36° at 106°; 18.06° at 120°.

$\alpha_{123.8}$ 41.50° at 21°; 39.30° at 41°; 37.90° at 57°; 36.48° at 72°; 33.90° at 93°; 32.42° at 106°; 31.14° at 119°.

* Whole cooling.

TABLE II.—(continued).

n-Hexyl.

Density 0.8845 at 28.5°; 0.8742 at 43°; 0.8562 at 67°; 0.8420 at 86°;
0.8230 at 108°; 0.7990 at 140°.
 α_{5893} 20.28° at 20.5°; 19.40° at 40°; 19.28° at 45.5°; 18.58° at 60°; 17.20°
at 93°; 16.26° at 123°.
 α_{5461} 24.08° at 20.5°; 22.80° at 40°; 21.64° at 59°; 20.68° at 74°; 19.70°
at 98°; 19.26° at 111°; 18.58° at 122.5°.
 α_{4358} 41.22° at 21°; 39.22° at 40°; 38.50° at 46°; 33.90° at 73.5°; 34.44° at
94°; 33.18° at 112°; 32.30° at 122.5°.

n-Heptyl.

Density 0.8816 at 27°; 0.8728 at 39°; 0.8430 at 82°; 0.8287 at 100°; 0.8167
at 116°; 0.8052 at 131.5°.
 α_{6439} 16.00° at 19°; 15.20° at 43°; 14.44° at 60°; 13.36° at 88.5°; 13.04°
at 111.5°; 12.18° at 134°.
 α_{5161} 22.90° at 19°; 21.70° at 44°; 20.00° at 71°; 19.22° at 89°; 18.14° at
111°; 17.32° at 134°.
 α_{5086} 26.98° at 19°; 25.48° at 44°; 24.00° at 62°; 22.78° at 88.5°; 21.52°
at 111.5°; 20.32° at 134°.
 α_{4800} 30.92° at 19°; 29.22° at 44°; 27.44° at 64°; 26.16° at 88°; 24.74° at
111°; 23.16° at 134°.
 α_{4678} 32.68° at 19°; 30.98° at 44.5°; 29.02° at 67°; 27.78° at 88°; 26.24° at
111°; 24.58° at 134°.
 α_{4358} 39.32° at 19°; 36.84° at 43°; 34.04° at 71°; 32.60° at 89°; 31.06° at
110.5°; 29.58° at 134°.

n-Octyl.

Density 0.8809 at 26°; 0.8700 at 41.5°; 0.8565 at 60°; 0.8397 at 84°;
0.8195 at 114°; 0.7981 at 142°.
 α_{6439} 15.26° at 20.5°; 14.64° at 32°; 14.28° at 54°; 13.46° at 71.5°; 12.98°
at 89°; 12.46° at 111.5°; 11.90° at 129°.
 α_{5461} 22.08° at 20.5°; 21.50° at 32°; 20.68° at 51°; 19.50° at 71°; 18.56° at
93°; 17.68° at 109°; 17.18° at 126°.
 α_{5086} 25.84° at 20.5°; 25.26° at 33°; 24.32° at 53°; 22.86° at 71°; 22.12° at
89°; 20.86° at 110°; 20.02° at 128.5°.
 α_{4800} 29.70° at 20.5°; 29.08° at 33.5°; 27.94° at 58.4°; 26.54° at 70°; 25.36°
at 90°; 24.04° at 109°; 23.10° at 128.2°.
 α_{4678} 31.54° at 20.5°; 30.82° at 35°; 29.56° at 51.6°; 28.10° at 69°; 26.78°
at 90.5°; 25.52° at 107°; 24.42° at 127°.
 α_{4358} 37.44° at 21°; 36.82° at 32°; 35.26° at 51°; 33.08° at 77°; 31.52° at
93°; 30.42° at 109.5°; 28.84° at 126°.

n-Nonyl.

Density 0.8822 at 25°; 0.8688 at 44°; 0.8561 at 63°; 0.8377 at 87.5°;
0.8128 at 122°; 0.7989 at 143°.
 α_{5893} 18.32° at 21°; 17.68° at 37.5°; 16.40° at 66°; 15.96° at 85.5°; 15.46°
at 98.5°; 15.10° at 111°*; 14.94° at 122°.
 α_{5461} 21.88° at 21°; 21.10° at 38°; 20.34° at 49°; 19.72° at 68.5°; 18.76° at
85°; 18.10° at 100°; 17.34° at 120°.
 α_{4358} 37.14° at 22°; 35.62° at 37.5°; 34.66° at 50°; 33.34° at 67.5°; 32.1°
at 85°*; 30.86° at 100°; 29.42° at 119°.

* While cooling.

TABLE II.
Ethers of d-Benzylmethylcarbinol.

[illegible]

TABLE IV.

Determinations of Rotatory Power in (approx.) 5 per cent. Ethyl Alcohol Solution.

Length of observation tube 20 cm. $T = 17^{\circ}$.

Ether.	Grams of substance in 100 c.c. of solution.	Observed rotation.					
		λ	λ	λ	λ	λ	λ
		5893.	5461.	4358.	5893.	5461.	4358.
Methyl	5.00	0.28°	0.49°	0.73°	2.8°	4.9°	7.3°
Ethyl	4.95	1.95	2.42	4.07	19.7	24.4	41.1
Propyl	5.01	2.11	2.41	4.14	21.1	24.0	41.3
Butyl	5.00	2.53	3.06	4.94	25.3	30.6	49.4
Amyl	4.91	2.52	3.06	5.02	25.6	31.1	51.1
Hexyl	5.04	2.57	3.09	5.06	25.5	30.7	50.3
Heptyl	5.07	2.51	3.02	5.00	24.8	29.8	49.3
Octyl	4.95	2.40	2.95	4.85	24.2	29.8	49.0
Nonyl	5.04	2.46	2.99	4.90	24.4	29.7	48.6

TABLE V.

Determinations of Rotatory Power in (approx.) 5 per cent. Carbon Disulphide Solution.

Length of observation tube 20 cm. $T = 17^{\circ}$.

Ether.	Grams of substance in 100 c.c. of solution.	Observed rotation.					
		λ	λ	λ	λ	λ	λ
		5893.	5461.	4358.	5893.	5461.	4358.
Methyl	5.00	3.62°	3.95°	8.13°	36.2°	39.5°	81.3°
Ethyl	5.01	4.45	5.15	9.45	44.4	51.4	94.3
Propyl	5.00	4.28	5.21	9.32	42.8	52.1	93.2
Butyl	4.98	4.26	5.28	9.49	42.7	53.0	95.2
Amyl	5.01	4.16	4.83	8.92	41.5	48.1	89.1
Hexyl	4.99	4.11	4.98	9.01	41.2	49.9	90.3
Heptyl	4.87	3.71	4.60	8.60	38.1	47.2	82.1
Octyl	5.05	3.82	4.60	8.26	37.9	45.6	81.9
Nonyl	4.96	3.72	4.43	8.00	37.5	44.6	80.6

Part of the expense of this investigation was defrayed by a grant from the Government Grant Committee of the Royal Society, and, in addition, the author wishes to express his thanks to the Department of Scientific and Industrial Research for a personal grant, and to Dr J. Kenyon and Mr H. Hunter for their interest and help.

BATTERSEA POLYTECHNIC, S.W. 11. [Received, November 1st, 1922.]

IV.—*Investigations on the Dependence of Rotatory Power on Chemical Constitution. Part XVI. The Di-d- β -octyl Esters of the Saturated Dicarboxylic Acids.*

By LESLIE HALL.

Among the results which emerge from this series of investigations are the interesting differences which have been observed in the optical rotatory and rotatory dispersive powers of aliphatic secondary alcohols and aliphatic ethers derived from them, on the one hand, and of aliphatic esters derived from the same alcohols, on the other.

Considering the rotatory powers first, it has been shown that those of the esters are, in general, much more susceptible to the influences of temperature, dissolution, and concentration than are those of the alcohols from which they are derived and of the ethers which may be derived from the same alcohols. Compare, for example, the differences in the temperature-rotation curves of *d-sec.*-octyl alcohol and of *d-sec.*-octyl acetate (Part I, T., 1911, 99, 50; Part V, T., 1914, 105, 837) and in the alterations in rotatory power which they respectively exhibit in certain solvents, notably carbon disulphide.

A legitimate deduction which may be drawn from a consideration of these and other facts is that the differences in behaviour shown by the esters may be due to some inherent property of the carbonyl group, and in order to obtain further evidence bearing on this point, a series of optically active esters derived from *d-sec.*-octyl alcohol and some saturated aliphatic normal dicarboxylic acids has been prepared and their optical behaviour investigated.

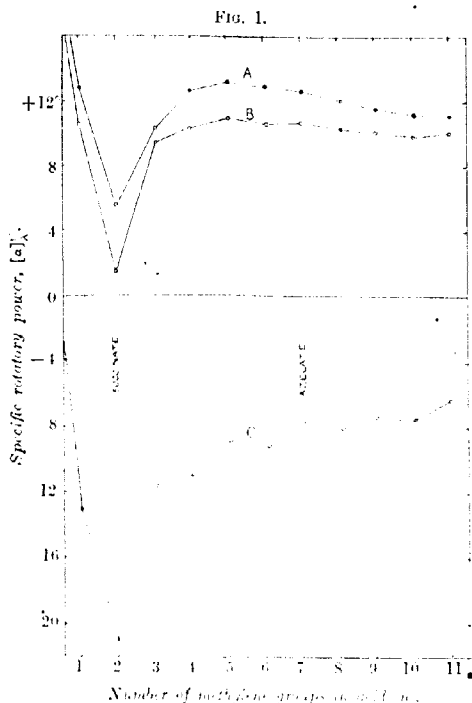
A series of optically active esters of aliphatic dibasic acids has been previously described in the literature by Walden (*J. Russ. Phys. Chem. Soc.*, 1898, 30, 767), who used the fermentation amyl alcohol; this, however, was not optically pure (compare Marckwald and McKenzie, *Ber.*, 1901, 34, 485), so that any deductions derived from a consideration of his results are unreliable.

Moreover, in this and other earlier work, the optical rotatory powers were determined for light of one wave-length only, and the measurements made only at the temperature of the laboratory.

The results of the polarimetric determinations tabulated on pp. 41 and 42, show that the esters herein described exhibit complex rotatory dispersion under all conditions employed, namely, in the homogeneous condition at temperatures from 20° to 130°.

and in solution in carbon disulphide and in ethyl alcohol at the ordinary temperature.

Not more than one ester, however, *d*,*g*-octyl succinate, was observed to exhibit anomalous rotatory dispersion in the region



The *d*,*g*-octyl esters of the dibasic acids $\alpha\text{H}_2\text{XCOOH}_4$.

- A, $[\alpha]_{\text{D}}^{20}$ in the homogeneous state.
 B, $[\alpha]_{\text{D}}^{20}$ in 5% solution in ethyl alcohol.
 C, $[\alpha]_{\text{D}}^{20}$ " " " " " carbon disulphide.

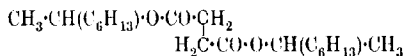
of the spectrum studied, and then only in 5 per cent. solution in ethyl alcohol at 18°.

An examination of the curves (Fig. 1) obtained by plotting the specific rotatory powers of the various esters against the number of methylene groups in the respective acids, shows:

(1) The oxalic ester possesses a particularly large optical rotation; a similar result was observed by Hilditch in the case of

l-menthyl oxalate (T., 1909, **95**, 1581), and the explanation of this given by Hilqitch, namely, that the contiguity of the two carboxyl groups in the oxalic acid residue is the cause of the exaltation in its esters, appears to be satisfactory.

(2) The succinic ester has a very small rotation. Now it has been observed in these series of investigations that chains of five, ten, fifteen, etc., atoms are often associated with peculiarities in optical behaviour. If the formula of this ester be written as follows,



it is apparent that there is the possibility of two chains containing five atoms or of two containing ten atoms, each influencing abnormally the magnitude of the optical rotatory power.

(3) The rotation values are alternately high and low as the series is ascended. This may be due to the alternate members of the oxalic acid series possessing a *cis*- or *trans*-configuration respectively. An analogous alternation is also known in a number of other physical properties of this series, for example, the melting points, solubility in water, solubility of the calcium salts, melting points of the methyl esters.

This view of the alternate *cis*- and *trans*-structure of this series has received support from the recent work of Irvine and Steele (T., 1915, **107**, 1221) and Price and Brazier (*ibid.*, **107**, 1719).

The latter authors, as a result of their work on the formation of additive compounds of complex metallic amines with these dicarboxylic acids, make the tentative suggestion that oxalic, succinic, and adipic acids possess a *trans*-configuration, whilst malonic and glutaric acids possess a *cis*-configuration. Such considerations on stereochemical grounds render untenable any assumption of the configuration of the succinic ester as containing chains of fifteen or twenty atoms, but it is suggested that the assumption of a configuration made up of two spirals agrees with the hypothesis advanced to account for the low rotation of the ester.

EXPERIMENTAL.

The active β -octanol required for the preparation of the esters was made by the method described by Kenyon (T., 1922, **121**, 2540).

Of the dibasic acids employed,* suberic and sebacic acids were obtained from Kahlbaum, whilst the others were prepared by the following methods:

Glutaric acid from trimethylene cyanide (Auger, *Ann. Chim. Phys.*, **1901**, [vi], **22**, 357).

Adipic acid by the oxidation of *cyclohexanol* with nitric acid (Bouveault and Locquin, *Bull. Soc. chim.*, 1908, [iv], **3**, 438).

Pimelic acid from trimethylene bromide and malonic ester (Blaise and Koehler, *ibid.*, 1909, [iv], **5**, 687).

Azelaic acid from castor oil (Maquenne, *ibid.*, 1899, [iii], **21**, 1061).

n-Nonane-, *n*-decane-, and *n*-undecane-dicarboxylic acids from undecenoic acid. The undecenoic acid was converted into ω -bromoundecenoic acid by the method of Walker and Lumsden (T., 1901, **79**, 1191). After a number of trials, it was ascertained that good yields of ω -bromoundecenoic acid can only be obtained by this method if the undecenoic acid is carefully purified beforehand by rapid distillation under diminished pressure.

The acid chlorides were prepared by mixing the pure dry acids with thionyl chloride (H. Meyer, *Monatsh.*, 1901, **22**, 421); the acid chlorides of the higher members of the series were not distilled owing to their instability at the high temperatures necessary.

d- β -Octyl oxalate was prepared by three methods: (i) by heating anhydrous oxalic acid with four times its weight of *d*- β -octyl alcohol at 150° for two hours followed by fractional distillation under diminished pressure; (ii) by heating ethyl oxalate with *d*- β -octyl alcohol (2 mols.) (a) at 175–180° for about ten hours in an uncorked flask, or (b) at 195–205° for about ten hours in a small aluminium autoclave, followed in each case by fractional distillation; (iii) by using methyl oxalate and working up the product as under (ii).

The following products were isolated as colourless liquids: *d*- β -octyl oxalate, b. p. 198–199°/11 mm., very faint odour; *d*- β -octyl ethyl oxalate, b. p. 138–140°/20 mm., fruity odour; and *d*- β -octyl methyl oxalate, b. p. 130–132°/20 mm., fruity odour.

d- β -Octyl malonate was prepared by method (ii) as described under the oxalate, using ethyl malonate, and also by method (i) with the modification that the mixture of malonic acid (7 grams) and *d*- β -octyl alcohol was treated with dry hydrogen chloride until 1 gram had been absorbed before it was heated at 100° for three hours. The reaction product was washed with sodium carbonate solution before distillation.

The following substances were isolated as colourless liquids: *d*- β -octyl malonate, b. p. 158–160°/19 mm., fruity odour; and *d*- β -octyl ethyl malonate, b. p. 198–200°/19 mm., fruity odour.

d- β -Octyl ethyl malonate was prepared also by the interaction of *d*- β -octyl alcohol and the acid chloride of ethyl hydrogen malonate.

TABLE II.
Molecular Refractive Powers $[\rho_L]_{589}^T$
of the Esters.

Ester.	Temp.	λ 6438.	λ 5896.	λ 5461.	λ 5086.	λ 4800.	λ 4678.	λ 4558.	D ₄ .	n_{589}^T	Observed $\frac{n^2-1}{n^2+2} \cdot \frac{M}{D_4}$	Difference from calc. value.
d-3-Octyl oxalate.	25.3	1.4369	1.4329	1.4317	1.4366	1.4385	1.4395	1.4426	0.9147	1.4329	89.27	+ 0.64
malonate.	25.2	1.4326	1.4315	1.4305	1.4384	1.4404	1.4412	1.4413	0.9150	1.4345	93.51	+ 0.26
succinate	25.8	1.4349	1.4367	1.4386	1.4407	1.4427	1.4432	1.4433	0.9127	1.4367	98.18	+ 0.31
glutarate	25.8	1.4365	1.4384	1.4401	1.4423	1.4441	1.4452	1.4497	0.9115	1.4384	102.69	+ 0.20
adipate	25.8	1.4402	1.4421	1.4421	1.4450	1.4470	1.4479	1.4509	0.9094	1.4402	107.36	+ 0.23
lino-late.	25.8	1.4392	1.4409	1.4429	1.4450	1.4470	1.4479	1.4509	0.9072	1.4409	111.75	+ 0.03
suberate	25.7	1.4406	1.4419	1.4439	1.4459	1.4476	1.4486	1.4516	0.9038	1.4419	116.59	+ 0.25
azelate	25.7	1.4412	1.4432	1.4450	1.4470	1.4490	1.4501	1.4532	0.9018	1.4432	121.27	+ 0.31
sebacate	25.8	1.4421	1.4441	1.4460	1.4479	1.4499	1.4511	1.4538	0.9000	1.4441	125.87	+ 0.29
n-nonane-a-di- carboxylate	25	1.4448	1.4468	1.4466				1.4545	0.8991	1.4448	130.31	+ 0.12
n-decane-a-di- carboxylate.	25.8	1.4453	1.4463	1.4485	1.4501	1.4521	1.4530	1.4560	0.8990	1.4463	134.56	- 0.25
l-undecan-a- dicarboxylate	25		1.4456	1.4475				1.4553	0.8938	1.4456	139.64	+ 0.21
d-3-Octyl methyl oxalate	25		1.4261	1.4289				1.4357	0.9790	1.4261	56.60	+ 0.30
ethyl oxalate	26	1.4234	1.4253	1.4277	1.4304	1.4311	1.4320	1.4348	0.9574	1.4253	61.50	+ 0.58
ethyl malonate	26	1.4219	1.4269	1.4286	1.4303	1.4323	1.4333	1.4361	0.9564	1.4269	65.35	- 0.19
l-3-Octyl methylsuccinate	25		1.4305	1.4323				1.4399	0.9629	1.4305	65.60	+ 0.06
d-3-Octyl ethylsuccinate	25.6	1.4289	1.4308	1.4326	1.4346	1.4364	1.4374	1.4402	0.9548	1.4308	69.96	- 0.20

TABLE I.
Refractive Indices (n_D) of the Esters.

TABLE III.

Observed Densities and Rotatory Powers of the Esters.

Rotations are here given as for a 1-dm. tube.

d- β -Octyl oxalate.

D_4^{25}	0.9147 at 26°; 0.9040 at 40.5°; 0.8863 at 63°; 0.8720 at 80.5°; 0.8563 at 100°.
α_{6893}	20.94° at 18.8°; 20.48° at 27.3°; 19.98° at 41°; 17.20° at 82°; 16.62° at 97°; 15.94° at 124°.
α_{5161}	24.52° at 18.8°; 23.78° at 27.5°; 21.64° at 49°; 19.84° at 80°; 18.86° at 97°; 17.98° at 130°.
α_{4358}	37.62° at 19.4°; 36.76° at 27.5°; 33.26° at 49°; 31.46° at 80°; 29.80° at 98°; 28.20° at 130°.

d- β -Octyl malonate.

D_4^{25}	0.9189 at 21.2°; 0.9005 at 45.5°; 0.8837 at 65°; 0.8706 at 80°; 0.8574 at 99°; 0.8395 at 122.5°.
α_{6138}	8.48° at 19.2°; 7.32° at 40°; 5.74° at 77°; 5.04° at 102°; 4.72° at 122°; 4.12° at 158°.
α_{5461}	11.76° at 19.2°; 10.24° at 41°; 8.16° at 76°; 7.04° at 100°; 6.34° at 122°; 5.72° at 158°.
α_{5086}	13.60° at 19.2°; 11.60° at 40°; 9.08° at 77°; 7.70° at 102°; 7.08° at 122°; 6.28° at 157°.
α_{4800}	15.18° at 19.2°; 12.86° at 40°; 10.62° at 77°; 8.56° at 102°; 7.86° at 122°; 6.72° at 157°.
α_{4678}	15.64° at 19.2°; 13.52° at 40°; 10.76° at 77°; 9.14° at 102°; 8.28° at 122°; 7.26° at 157°.
α_{4358}	17.82° at 19.2°; 15.02° at 41°; 11.86° at 76°; 10.12° at 100°; 9.66° at 122°; 7.72° at 158°.

d- β -Octyl succinate.

D_4^{25}	0.9175 at 19.7°; 0.8982 at 44.5°; 0.8853 at 60.3°; 0.8700 at 81.2°; 0.8511 at 107°; 0.8405 at 120.5°; 0.8222 at 142°; 0.8072 at 162.5°.
α_{6138}	3.76° at 19.2°; 3.36° at 57°; 3.14° at 81°; 3.16° at 128°; 3.14° at 144°.
α_{5461}	5.04° at 19.2°; 4.64° at 56°; 4.14° at 82°; 4.26° at 126°; 4.06° at 144°.
α_{5086}	5.48° at 19.2°; 4.86° at 57°; 4.50° at 81°; 4.61° at 128°; 4.56° at 144°.
α_{4800}	6.12° at 19.2°; 5.28° at 59°; 4.96° at 81°; 4.94° at 128°; 4.88° at 144°.
α_{4678}	6.46° at 19.2°; 5.60° at 59°; 5.44° at 81°; 5.30° at 128°; 5.12° at 144°.
α_{4358}	7.02° at 19.2°; 6.02° at 56°; 5.72° at 81°; 5.56° at 126°; 5.52° at 144°.

d- β -Octyl glutarate.

D_4^{25}	0.9204 at 17°; 0.9040 at 35.5°; 0.8921 at 50.5°; 0.8688 at 82.5°; 0.8543 at 100°; 0.8358 at 124°; 0.8213 at 143°; 0.8035 at 164°.
α_{6138}	6.70° at 17°; 5.92° at 37.6°; 4.70° at 69°; 4.14° at 98°; 3.80° at 125°; 3.52° at 147°.
α_{5461}	9.78° at 17°; 8.32° at 37.2°; 6.84° at 68°; 5.78° at 99°; 5.24° at 122°; 4.74° at 148°.
α_{5086}	10.88° at 17°; 9.52° at 37.6°; 7.48° at 69°; 6.52° at 98°; 5.62° at 125°; 5.42° at 147°.
α_{4800}	12.12° at 17°; 10.50° at 37.6°; 8.22° at 69°; 7.18° at 98°; 6.56° at 125°; 6.08° at 147°.
α_{4678}	12.60° at 17°; 11.02° at 37.6°; 8.70° at 69°; 7.56° at 98°; 6.98° at 125°; 6.38° at 147°.
α_{4358}	14.88° at 17°; 12.38° at 37.2°; 10.04° at 68°; 8.68° at 99°; 8.00° at 122°; 7.12° at 148°.

d- β -Octyl adipate.

D_4^I	0-9072 at 28°; 0-8933 at 46-25°; 0-8774 at 68°; 0-8602 at 90-5°; 0-8371 at 121°.
α_{5993}	10-20° at 19-8°; 9-90° at 28-5°; 8-50° at 60°; 7-36° at 85°; 6-74° at 108°; 6-02° at 121°.
α_{5161}	11-58° at 19-8°; 11-14° at 28-5°; 9-34° at 59°; 8-42° at 84°; 7-24° at 108°; 6-86° at 129°.
α_{1253}	18-20° at 19-8°; 17-32° at 28-5°; 15-10° at 59°; 13-28° at 84°; 11-46° at 108°; 10-86° at 122°.

d- β -Octyl pimelate.

D_4^I	0-9111 at 21°; 0-8948 at 41-5°; 0-8792 at 63-5°; 0-8666 at 80-5°; 0-8519 at 99-5°; 0-8347 at 123°; 0-8181 at 143°; 0-8058 at 161°.
α_{6138}	8-68° at 19-5°; 7-76° at 37-2°; 6-32° at 73-5°; 5-78° at 97°; 5-10° at 127°; 4-68° at 145°.
α_{5161}	12-02° at 19-5°; 10-38° at 39°; 8-32° at 73-5°; 7-58° at 99-2°; 6-78° at 126°; 6-20° at 145°.
α_{5993}	14-00° at 19-5°; 12-40° at 38°; 9-70° at 76°; 8-70° at 97°; 8-08° at 127°; 7-44° at 145°.
α_{1305}	15-63° at 19-5°; 13-78° at 38°; 10-62° at 74°; 9-02° at 97°; 9-02° at 127°; 8-02° at 145°.
α_{1678}	16-60° at 19-5°; 14-22° at 39°; 11-06° at 73°; 10-58° at 97°; 9-52° at 127°; 9-00° at 145°.
α_{1253}	18-80° at 19-5°; 16-02° at 40°; 12-86° at 73°; 11-54° at 99-2°; 10-60° at 126°; 10-04° at 145°.

d- β -Octyl suberate.

D_4^I	0-9084 at 20°; 0-8925 at 41°; 0-8788 at 60-7°; 0-8640 at 80-5°; 0-8492 at 100°; 0-8285 at 128°.
α_{5993}	9-80° at 22-6°; 8-92° at 49°; 7-56° at 76°; 6-56° at 92°; 6-06° at 102°; 5-56° at 127°.
α_{5161}	11-56° at 22-6°; 10-04° at 48°; 8-42° at 75°; 7-76° at 92°; 7-56° at 102°; 7-14° at 127°.
α_{1353}	17-58° at 22-6°; 15-50° at 48°; 14-26° at 75°; 12-92° at 92°; 12-08° at 102°; 10-72° at 127°.

d- β -Octyl azelate.

D_4^I	0-9053 at 20°; 0-8908 at 40-8°; 0-8768 at 60-7°; 0-8640 at 80°; 0-8486 at 100°; 0-8324 at 121°; 0-8191 at 142°; 0-8037 at 163°; 0-7874 at 185°; 0-7695 at 210°.
α_{6138}	8-18° at 19-4°; 6-94° at 51-7°; 6-48° at 67°; 5-98° at 95°; 5-30° at 107°; 4-88° at 129°.
α_{5161}	11-66° at 19-4°; 9-94° at 45°; 8-98° at 67°; 8-26° at 80°; 7-80° at 95°; 7-62° at 107°; 7-04° at 129°.
α_{5993}	13-28° at 19-4°; 11-52° at 51-7°; 10-36° at 67°; 9-98° at 80°; 8-94° at 95°; 8-58° at 107°; 7-52° at 129°.
α_{1305}	14-76° at 19-4°; 12-62° at 51-2°; 11-50° at 67°; 10-90° at 80°; 9-94 at 95°; 9-38° at 107°; 8-40° at 129°.
α_{1678}	15-40° at 19-4°; 12-92° at 51-7°; 11-98° at 67°; 11-24° at 80°; 10-24 at 95°; 9-82° at 107°; 8-68° at 129°.
α_{1253}	17-96° at 19-4°; 15-12° at 47°; 13-56° at 67°; 13-08° at 80°; 11-90° at 95°; 11-68° at 107°; 10-52° at 129°.

d-β-Octyl sebacate.

D_4^D 0.0935 at 20.6°; 0.8898 at 39.8°; 0.8730 at 79°; 0.8474 at 99.8°; 0.8205 at 123°; 0.8137 at 146°; 0.8019 at 163°.
 α_{6138} 7.98° at 18.8°; 6.38° at 48.8°; 5.46° at 78°; 4.88° at 99°; 4.64° at 128°; 4.12° at 152°.
 α_{5161} 10.86° at 18.8°; 9.34° at 51°; 7.56° at 77.5°; 6.50° at 106°; 5.94° at 130°; 5.26° at 155°.
 α_{5086} 12.84° at 18.8°; 10.58° at 48.8°; 8.88° at 78°; 7.84° at 100°; 7.04° at 128°; 6.42° at 152°.
 α_{4893} 14.36° at 18.8°; 11.64° at 48.8°; 9.62° at 79°; 8.80° at 101°; 7.56° at 128°.
 α_{4476} 15.28° at 18.8°; 12.30° at 48.8°; 9.88° at 80°; 8.88° at 102°; 8.42° at 128°.
 α_{4358} 17.16° at 18.8°; 13.72° at 51°; 12.00° at 77.5°; 9.94° at 106°; 9.10° at 130.5°; 8.70° at 155°.

d-β-Octyl *n*-nonane- α -dicarboxylate.

D_4^D 0.8991 at 25°; 0.8839 at 46°; 0.8744 at 61.5°; 0.8612 at 79°; 0.8463 at 98°.
 α_{4922} 9.36° at 20°; 8.42° at 37°; 8.04° at 48.2°; 7.46° at 65°; 6.98° at 81°; 5.96° at 103°; 5.26° at 120°; 4.64° at 132°.
 α_{5161} 10.64° at 20°; 9.50° at 37°; 8.84° at 47°; 8.26° at 65°; 7.62° at 81°; 6.70° at 97°; 6.02° at 118°; 5.34° at 132°.
 α_{4358} 16.58° at 20°; 14.48° at 37°; 13.58° at 47°; 12.68° at 65°; 11.58° at 81°; 10.58° at 97°; 8.90° at 120°; 8.22° at 132°.

d-β-Octyl *n*-decane- α -dicarboxylate.

D_4^D 0.8960 at 30°; 0.8816 at 50.5°; 0.8678 at 69°; 0.8543 at 89°; 0.8266 at 124°; 0.8110 at 142°.
 α_{5393} 9.38° at 20.2°; 8.24° at 35°; 7.60° at 54°; 6.94° at 71°; 6.26° at 85°; 5.92° at 99°; 5.60° at 120°.
 α_{5161} 10.22° at 20.2°; 9.68° at 33°; 8.40° at 54°; 7.96° at 71°; 7.24° at 85°; 6.70° at 99°; 6.16° at 120°; 5.90° at 133°.
 α_{4358} 15.38° at 20.2°; 14.20° at 33°; 12.80° at 54°; 12.00° at 71°; 11.32° at 85°; 10.72° at 99°; 9.70° at 120°.

d-β-Octyl *n*-undecane- α -dicarboxylate.

D_4^D 0.8894 at 31°; 0.8746 at 51°; 0.8606 at 70°; 0.8468 at 90°; 0.8231 at 120°; 0.8021 at 142°.
 α_{5893} 8.28° at 21°; 7.94° at 32°; 7.52° at 49°; 7.32° at 71°; 6.86° at 95°; 6.66° at 110°; 6.26° at 126°.
 α_{5461} 9.96° at 21°; 9.44° at 32°; 8.90° at 50°; 8.16° at 71°; 7.58° at 95°; 7.00° at 110°; 6.68° at 126°.
 α_{4358} 15.66° at 21°; 14.46° at 32°; 13.50° at 50°; 12.48° at 71°; 11.66° at 95°; 10.14° at 110°; 9.66° at 126°.

d-β-Octyl methyl oxalate.

D_4^D 0.9745 at 30°; 0.8563 at 50°; 0.9380 at 70.5°; 0.9183 at 90°; 0.8894 at 119°; 0.8636 at 140°.
 α_{5893} 14.04° at 19°; 13.08° at 34°; 11.90° at 64°; 11.14° at 90°; 10.24° at 112°; 9.56° at 126°.
 α_{5461} 16.54° at 19°; 15.04° at 35°; 14.00° at 60°; 12.38° at 90°; 11.44° at 112°; 10.74° at 126°.
 α_{4358} 25.72° at 19°; 24.00° at 34°; 22.10° at 59°; 19.62° at 90°; 18.68° at 112°; 17.42° at 126°.

d- β -Octyl ethyl oxalate.

D_4^D 0.9574 at 26.5°; 0.9428 at 43°; 0.9251 at 62.5°; 0.9067 at 82°.
 α_{5895} 13.20° at 24°; 11.88° at 53°; 11.58° at 73°; 11.08° at 96°; 10.84° at 116°.
 α_{5461} 15.40° at 24°; 13.60° at 53°; 12.62° at 73°; 12.14° at 96°; 11.60° at 116°.
 α_{4358} 23.68° at 24°; 21.24° at 53°; 19.46° at 73°; 18.08° at 96°; 16.98° at 116°.

d β -Octyl ethyl malonate.

D_4^D 0.9519 at 28°; 0.9328 at 49°; 0.9175 at 68°; 0.8867 at 100.5°.
 α_{5895} 8.82° at 21.5°; 7.86° at 35°; 7.02° at 54°; 6.24° at 75°; 5.90° at 92°; 5.18° at 108°.
 α_{5461} 10.38° at 21.5°; 9.16° at 35°; 7.92° at 55°; 7.18° at 75°; 6.64° at 93°; 5.78° at 111°.
 α_{4358} 16.52° at 21.5°; 14.94° at 35°; 13.02° at 55°; 11.84° at 75°; 10.64° at 93°; 8.86° at 110°.

l- β -Octyl methyl succinate.

D_4^D 0.9627 at 25°; 0.9508 at 39.5°; 0.9330 at 60°; 0.9164 at 80°; 0.8989 at 100°; 0.8782 at 123°.
 α_{5895} -3.42° at 19.5°; -3.32° at 36°; -3.12° at 58°; -2.88° at 84°; -2.58° at 106°; -2.38° at 126°.
 α_{5461} -3.84° at 19.5°; -3.76° at 34°; -3.46° at 58°; -3.14° at 86°; -2.84° at 106°; -2.56° at 125°.
 α_{4358} -5.64° at 19.5°; -5.46° at 35°; -5.04° at 58°; -4.64° at 86°; -4.34° at 106°; -4.08° at 125°.

d- β -Octyl ethyl succinate.

D_4^D 0.9614 at 17.4°; 0.9434 at 39.5°; 0.9223 at 63.3°; 0.9090 at 79°; 0.8904 at 102°; 0.8746 at 123°.
 α_{5133} 2.40° at 18.2°; 2.24° at 30.2°; 2.16° at 52°; 2.06° at 79°; 1.94° at 107°; 1.64° at 124°.
 α_{5461} 3.58° at 18.2°; 3.36° at 30.5°; 3.22° at 51°; 3.06° at 80°; 2.80° at 107°; 2.76° at 126°.
 α_{5056} 3.84° at 18.2°; 3.68° at 30.2°; 3.46° at 52°; 3.20° at 78°; 2.92° at 107°; 2.92° at 121°.
 α_{1300} 4.24° at 18.2°; 4.08° at 30.2°; 3.72° at 52°; 3.50° at 78°; 3.40° at 107°; 3.22° at 121°.
 α_{1478} 4.42° at 18.2°; 4.28° at 30.2°; 3.92° at 52°; 3.74° at 78°; 3.68° at 107°.
 α_{1354} 5.22° at 18.2°; 4.90° at 30.5°; 4.58° at 51°; 4.28° at 80°; 4.08° at 107°.

d- β -Octyl succinate was prepared by method (ii) using ethyl succinate, by method (iii) using methyl succinate, and also by the interaction of succinyl chloride and *d*- β -octyl alcohol.

The products obtained were: *d*- β -octyl succinate, b. p. 208–211°/16 mm., very faint odour; *d*- β -octyl ethyl succinate, b. p. 160–162°/16 mm., fruity odour; and *l*- β -octyl methyl succinate, b. p. 163–164°/15 mm., fruity odour.

The remaining esters were obtained by the interaction of *d*- β -octyl alcohol and the required acid chloride as colourless, somewhat viscous, almost odourless liquids and possessed the following boiling points: glutarate, b. p. 175–177°/3 mm.; adipate, b. p. 175°/2 mm.; pimelate, b. p. 188–190°/3 mm.; suberate, b. p. 202–204°/3 mm.; azelate, b. p. 208–210°/2 mm.; sebacate, b. p. 240–242°/7 mm.; *n*-nonanedicarboxylate, b. p. 205–207°/1 mm.; *n*-dodecicarboxylate, b. p. 205–207°/1 mm.

TABLE IV.
Densities and Rotatory Powers of the Esters.

<i>d.β-Octyl oxalate.</i>									
<i>t.</i>	<i>D₂₀²⁰</i>	<i>a_D²⁰</i>	<i>a_L²⁰</i>	<i>a_L²⁵</i>	<i>a_L³⁰</i>	<i>D₂₀²⁰</i>	<i>a_D²⁰</i>	<i>a_L²⁰</i>	<i>a_L²⁵</i>
20	0.9198	22.72	26.50	40.66	0.9168	9.19	12.83	14.79	16.37
40	0.9043	21.56	24.93	38.77	0.9038	8.08	11.33	12.88	14.23
60	0.8884	20.60	23.72	37.15	0.8863	7.09	10.18	11.44	12.68
80	0.8725	19.86	22.83	35.96	0.8729	6.42	9.17	10.24	11.39
100	0.8561	19.32	22.26	34.92	0.8574	5.95	8.40	9.33	10.29
120	0.8397	18.98	21.77	34.00	0.8424	5.51	7.76	8.62	9.43
<i>d.β-Octyl succinate.</i>									
<i>t.</i>	<i>D₂₀²⁰</i>	<i>a_D²⁰</i>	<i>a_L²⁰</i>	<i>a_L²⁵</i>	<i>a_L³⁰</i>	<i>D₂₀²⁰</i>	<i>a_D²⁰</i>	<i>a_L²⁰</i>	<i>a_L²⁵</i>
20	0.9171	4.98	5.54	6.00	6.65	7.02	7.34	7.12	7.33
40	0.9017	3.93	5.32	5.77	6.39	6.50	7.23	6.33	6.53
60	0.8861	3.77	5.21	5.60	6.21	6.30	7.04	6.09	6.29
80	0.8710	3.63	5.10	5.49	6.04	6.09	6.82	5.87	6.07
100	0.8555	3.52	5.03	5.45	5.96	6.02	6.69	5.82	6.02
120	0.8393	3.33	5.03	5.43	5.91	6.12	6.41	5.63	5.83
<i>d.β-Octyl adipate.</i>									
<i>t.</i>	<i>D₂₀²⁰</i>	<i>a_D²⁰</i>	<i>a_L²⁰</i>	<i>a_L²⁵</i>	<i>a_L³⁰</i>	<i>D₂₀²⁰</i>	<i>a_D²⁰</i>	<i>a_L²⁰</i>	<i>a_L²⁵</i>
20	0.9135	11.23	12.66	16.93	0.9105	9.53	13.18	15.33	17.22
40	0.8984	10.12	11.61	18.34	0.8954	8.49	11.52	13.34	14.10
60	0.8832	9.55	10.69	16.93	0.8810	7.72	10.31	11.83	13.39
80	0.8682	8.69	9.81	15.32	0.8666	7.13	9.42	10.80	12.28
100	0.8530	7.90	9.01	14.23	0.8518	6.76	8.83	10.14	11.62
120	0.8380	7.19	8.23	13.17	0.8363	6.53	8.44	9.66	11.26
<i>d.β-Octyl sebacate.</i>									
<i>t.</i>	<i>D₂₀²⁰</i>	<i>a_D²⁰</i>	<i>a_L²⁰</i>	<i>a_L²⁵</i>	<i>a_L³⁰</i>	<i>D₂₀²⁰</i>	<i>a_D²⁰</i>	<i>a_L²⁰</i>	<i>a_L²⁵</i>
20	0.9084	11.01	12.95	19.59	0.9050	9.08	12.76	14.69	16.36
40	0.8937	9.80	11.59	17.97	0.8912	8.37	11.58	13.51	14.99
60	0.8789	8.87	10.47	16.77	0.8770	7.75	10.68	12.36	13.69
80	0.8642	8.03	9.54	15.79	0.8627	7.16	9.85	11.33	12.57
100	0.8493	7.35	8.95	14.84	0.8485	6.64	9.17	10.40	11.50
120	0.8346	6.85	8.46	13.88	0.8340	6.23	8.58	9.59	10.60
<i>d.β-Octyl pimelate.</i>									
<i>t.</i>	<i>D₂₀²⁰</i>	<i>a_D²⁰</i>	<i>a_L²⁰</i>	<i>a_L²⁵</i>	<i>a_L³⁰</i>	<i>D₂₀²⁰</i>	<i>a_D²⁰</i>	<i>a_L²⁰</i>	<i>a_L²⁵</i>
20	0.9135	11.23	12.66	16.93	0.9105	9.53	13.18	15.33	17.22
40	0.8984	10.12	11.61	18.34	0.8954	8.49	11.52	13.34	14.10
60	0.8832	9.55	10.69	16.93	0.8810	7.72	10.31	11.83	13.39
80	0.8682	8.69	9.81	15.32	0.8666	7.13	9.42	10.80	12.28
100	0.8530	7.90	9.01	14.23	0.8518	6.76	8.83	10.14	11.62
120	0.8380	7.19	8.23	13.17	0.8363	6.53	8.44	9.66	11.26
<i>d.β-Octyl glutarate.</i>									
<i>t.</i>	<i>D₂₀²⁰</i>	<i>a_D²⁰</i>	<i>a_L²⁰</i>	<i>a_L²⁵</i>	<i>a_L³⁰</i>	<i>D₂₀²⁰</i>	<i>a_D²⁰</i>	<i>a_L²⁰</i>	<i>a_L²⁵</i>
20	0.9171	4.98	5.54	6.00	6.65	7.02	7.34	7.12	7.33
40	0.9017	3.93	5.32	5.77	6.39	6.50	7.23	6.33	6.53
60	0.8861	3.77	5.21	5.60	6.21	6.30	7.04	6.09	6.29
80	0.8710	3.63	5.10	5.49	6.04	6.09	6.82	5.87	6.07
100	0.8555	3.52	5.03	5.45	5.96	6.02	6.69	5.82	6.02
120	0.8393	3.33	5.03	5.43	5.91	6.12	6.41	5.63	5.83
<i>d.β-Octyl azelate.</i>									
<i>t.</i>	<i>D₂₀²⁰</i>	<i>a_D²⁰</i>	<i>a_L²⁰</i>	<i>a_L²⁵</i>	<i>a_L³⁰</i>	<i>D₂₀²⁰</i>	<i>a_D²⁰</i>	<i>a_L²⁰</i>	<i>a_L²⁵</i>
20	0.9084	11.01	12.95	19.59	0.9050	9.08	12.76	14.69	16.36
40	0.8937	9.80	11.59	17.97	0.8912	8.37	11.58	13.51	14.99
60	0.8789	8.87	10.47	16.77	0.8770	7.75	10.68	12.36	13.69
80	0.8642	8.03	9.54	15.79	0.8627	7.16	9.85	11.33	12.57
100	0.8493	7.35	8.95	14.84	0.8485	6.64	9.17	10.40	11.50
120	0.8346	6.85	8.46	13.88	0.8340	6.23	8.58	9.59	10.60

TABLE IV (continued).
Densities and Rotatory Powers of the Esters.

<i>d</i> -β-Octyl sebacate.				<i>d</i> -β-Octyl <i>n</i> -nonic- α -dicarboxylate.				<i>d</i> -β-Octyl <i>n</i> -decane- α -dicarboxylate.				
<i>t</i> , °	<i>D</i> _D ²⁰	α _D ²⁰	$[\alpha]$ _D ²⁰	<i>D</i> _D ²⁰	α _D ²⁰	$[\alpha]$ _D ²⁰	<i>D</i> _D ²⁰	α _D ²⁰	$[\alpha]$ _D ²⁰	<i>D</i> _D ²⁰	α _D ²⁰	$[\alpha]$ _D ²⁰
20°	0.89038	8.45	12.04	14.16	15.80	18.87°	0.9027	10.37°	11.75°	18.30°	0.9031	10.36°
40°	0.8897	7.64	10.84	12.75	14.03	16.86	0.8862	9.39	10.54	16.05	0.8887	9.25
60°	0.8752	6.95	9.76	11.43	12.48	15.04	8.63	9.66	14.65	14.65	0.8744	8.42
80°	0.8611	6.39	8.83	10.36	11.29	13.71	8.03	8.87	13.43	13.43	0.8599	7.67
100°	0.8470	5.95	8.03	9.49	10.34	11.10	7.29	8.05	12.33	12.33	0.8455	7.02
120°	0.8326	5.62	7.45	8.72	9.61	10.31	6.29	7.18	11.27	11.27	0.8307	6.52
<i>d</i> -β-Octyl <i>n</i> -undecane- α -dicarboxylate.				<i>d</i> -β-Octyl methyl oxalate.				<i>d</i> -β-Octyl ethyl oxalate.				
<i>t</i> , °	<i>D</i> _D ²⁰	α _D ²⁰	$[\alpha]$ _D ²⁰	<i>D</i> _D ²⁰	α _D ²⁰	$[\alpha]$ _D ²⁰	<i>D</i> _D ²⁰	α _D ²⁰	$[\alpha]$ _D ²⁰	<i>D</i> _D ²⁰	α _D ²⁰	$[\alpha]$ _D ²⁰
20°	0.8975	9.25	11.12	17.45°	0.9840	14.22	16.64°	0.9638	13.98°	16.33°	0.9631	16.33°
40°	0.8827	8.77	10.35	16.02	0.9656	13.32	15.24	0.9453	13.05	15.13	0.9453	15.13
60°	0.8680	8.48	9.75	14.79	0.9471	12.72	14.42	0.9269	12.54	14.17	0.9269	14.17
80°	0.8533	8.27	9.33	13.78	0.9285	12.22	13.77	0.9085	12.48	13.72	0.9085	13.72
100°	0.8386	8.02	8.95	12.83	0.9100	11.79	13.21	0.8902	12.38	13.44	0.8902	13.44
120°	0.8237	7.89	8.74	11.99	0.8915	11.39	12.68	0.8718	12.37	13.36	0.8718	13.36
<i>d</i> -β-Octyl ethyl malonate.				<i>d</i> -β-Octyl methyl succinate.				<i>d</i> -β-Octyl ethyl succinate.				
<i>t</i> , °	<i>D</i> _D ²⁰	α _D ²⁰	$[\alpha]$ _D ²⁰	<i>D</i> _D ²⁰	α _D ²⁰	$[\alpha]$ _D ²⁰	<i>D</i> _D ²⁰	α _D ²⁰	$[\alpha]$ _D ²⁰	<i>D</i> _D ²⁰	α _D ²⁰	$[\alpha]$ _D ²⁰
20°	0.9596	9.27	10.83	17.40°	0.9672	13.54	15.97°	0.9600	13.47°	15.97°	0.9600	15.97°
40°	0.9415	8.10	9.28	15.19	0.9501	13.30	15.42	0.9425	13.29	15.42	0.9425	15.42
60°	0.9234	7.36	8.41	13.74	0.9331	13.04	15.00	0.9252	13.25	15.00	0.9252	15.00
80°	0.9054	6.67	7.73	12.59	0.9160	12.79	14.58	0.9080	13.00	14.58	0.9080	14.58
100°	0.8872	6.13	7.17	11.61	0.8991	12.54	14.16	0.8912	12.80	14.16	0.8912	14.16
120°	0.8691	5.66	6.72	10.81	0.8822	12.27	13.74	0.8740	12.80	13.74	0.8740	13.74

TABLE V.
Determinations of Rotatory Power in approximately 5 per cent. Solution.

Ester.	In ethyl alcohol.				In carbon disulphide.			
	Grams of ester in 100 c.c. of solution.	Temp.	α_{589}	α_{589}	Grams of ester in 100 c.c. of solution.	Temp.	α_{589}	α_{589}
<i>d</i> . β . Octyl oxalate.	4.99	18	2.37	4.36	23.73	27.51	43.66 ⁵	4.97
undecinate	5.04	"	0.97	1.66	1.92	9.63	16.97	4.99
succinate	5.10	"	0.18	0.17	-0.03	1.77	-0.29	5.03
glutarate	5.07	"	0.85	0.96	1.47	8.39	14.51	5.03
adipate	5.03	"	0.95	1.04	1.68	9.45	16.72	5.11
pimelate	5.04	"	0.95	1.11	1.81	9.43	11.03	5.09
suberate	5.03	19	0.90	1.08	1.78	8.95	10.71	5.01
azelate	5.15	"	0.95	1.12	1.66	9.22	10.86	5.03
sebacate	5.00	18	0.87	1.04	1.68	8.71	10.41	4.96
<i>n</i> . β . α . Dicarboxylic.	5.04	"	0.80	1.02	1.65	8.93	10.12	4.97
<i>n</i> . β . α . α . Dicarboxylic.	5.04	19	0.92	1.00	1.66	9.29	9.98	4.97
<i>n</i> . β . α . α . α . Dicarboxylic.	4.92	"	0.87	0.93	1.40	9.41	10.66	4.71
<i>d</i> . β . Octyl methyl oxalate.	4.95	20	1.39	1.61	2.31	13.14	16.28	4.57
ethyl oxalate	4.99	18	1.36	1.80	2.26	13.61	18.03	5.01
ethyl malonate	5.04	21	0.74	0.82	1.38	7.34	8.14	5.06
<i>d</i> . β . α . α . α . Methyl succinate	5.02	20	0.13	0.22	-0.30	-1.29	-2.18	5.06
ethyl succinate	5.07	18	0.19	0.27	0.48	1.87	2.66	4.99

oxylate, b. p. 205—210°/1 mm.; and *n*-undecanedicarboxylate, b. p. 215—217°/2 mm.

The last ester in the list solidified on keeping to a mass of colourless plates which melt at 21°.

The esters were not analysed in the usual way, as agreement between the experimentally determined and the calculated values of the molecular refraction was considered to be a more satisfactory criterion of purity.

Density determinations were carried out between 20° and 130°, a carefully calibrated pycnometer of about 3 c.c. capacity being used.

Refractive indices were determined at a constant temperature for light of several wave-lengths by means of a refractometer of the Pulfrich type.

The polarimetric measurements were made in a 50 mm. jacketed tube round which mineral oil was circulated by means of a pump. Observations were made from 20° to about 140° at temperature intervals of about 20°, but in Table III rotations are given as for a 1-dm. tube.

That no racemisation had occurred during the preparation of the esters or during their subsequent heating or treatment with solvents was proved by the fact that all the esters on subsequent hydrolysis yielded *sec*-octyl alcohol of maximum rotation.

For observations of rotatory power in solution, about 1 gram of the active ester was dissolved in the solvent and the solution made up to 20 c.c. at the temperature of the laboratory. Determinations of rotatory power were made in a 2-dm. tube.

The author wishes to express his thanks to the Department of Scientific and Industrial Research for a maintenance grant which has enabled him to carry out this work, and also to Dr. J. Kenyon and Mr. H. Hunter for their interest and guidance.

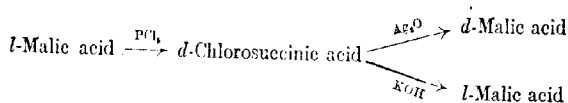
BATTERSEA POLYTECHNIC, S.W. 11. [Received, November 1st, 1922.]

V.—*Investigations on the Dependence of Rotatory Power on Chemical Constitution. Part XVII. A New Type of Walden Inversion.*

By HENRY PHILLIPS.

IN the examples of the Walden inversion so far recorded, an entire group attached to the asymmetric carbon atom of an optically active compound suffers two or more displacements. By this

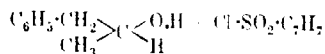
means either the same compound of opposite configuration is obtained or, by conducting one displacement under two different sets of conditions, products are obtained which are opposite in sign :



The above scheme, due to Walden (*Ber.*, 1896, **29**, 113), illustrates both types. They are, therefore, processes occurring in two stages. At one of these stages an "abnormal" reaction occurs resulting in a change of configuration, but at which one it is impossible to decide. In both reactions a group attached to the asymmetric carbon atom is replaced. Does the entering group in the first displacement take up the same position relative to the three remaining groups as that vacated by the group displaced? The sign of rotation of the product cannot be relied upon to give a correct answer to this question. Many instances are known in which substitution occurs remote from the asymmetric carbon atom, yet produces a reversal of sign. In such cases no change of configuration can be assumed, and therefore it is evident that change of sign does not necessarily coincide with change of configuration.

Attempts have been made to overcome this difficulty and to provide a method of determining whether a given reaction is abnormal from a consideration of the mechanism of the reactions in question by, *inter alios*, Armstrong (*T.*, 1896, **69**, 1399), Gadamer (*Chem. Ztg.*, 1910, **34**, 1004), and Biilmann (*Annalen*, 1911, **388**, 338). Further, Clough (*T.*, 1918, **113**, 526) has suggested certain principles by which the relative configurations of similarly constituted compounds can be determined.

In the examples of the Walden inversion to be described, however, we can on general grounds single out the particular reactions which occur with configurational change. When *d*-benzylmethylcarbinol is allowed to react with *p*-toluenesulphonyl chloride in the presence of pyridine, benzylmethylcarbinyl *p*-toluenesulphonate is obtained.

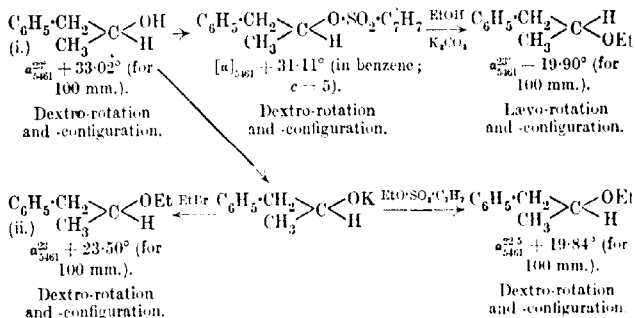


In this reaction, complete substitution of a group attached to the asymmetric carbon atom does not occur, the hydrogen atom of the hydroxyl group alone suffers displacement. It is justifiable

therefore, to refer to the sulphonic ester prepared in this way from the dextrorotatory alcohol as the *d*-sulphonate, and it is interesting to note that when this is dissolved in benzene, chloroform, ethyl alcohol, carbon disulphide, or pyridine, the solutions obtained are all dextrorotatory.

When this *d*-sulphonate is treated with sodium ethoxide in benzene or, better, heated under reflux in absolute alcoholic solution in the presence of solid potassium carbonate, the ethyl ether of benzylmethylcarbinol is formed and has in this case a levo-rotation.

If, however, *d*-benzylmethylcarbinol be converted into its potassium derivative and the latter allowed to react with ethyl *p*-toluenesulphonate, the ethyl ether of benzylmethylcarbinol produced has a dextrorotation.



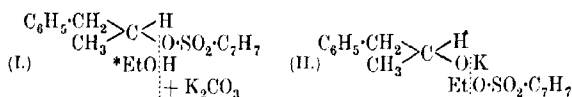
What is the sign of rotation of the ethyl ether which corresponds in configuration to the *d*-alcohol? This can be decided by the fact that the potassium derivative of the *d*-alcohol gives a dextrorotatory ethyl ether when treated with ethyl bromide, a reaction in which configurative change is unlikely to occur.

In the first series of reactions, however, the levorotatory ethyl ether of benzylmethylcarbinol is obtained from the dextrorotatory sulphonate, which can be said to have the same configuration as *d*-benzylmethylcarbinol. The conclusion can therefore be drawn that when the dextrorotatory sulphonate reacts with ethyl alcohol in the presence of potassium carbonate, the *l*-ethyl ether of benzylmethylcarbinol is produced, the configuration of which is the opposite to that of the dextrorotatory sulphonate used.

This is a definite change in configuration in one stage and therefore it is a definitely "abnormal" reaction.

How does this conclusion agree with the usually adopted views

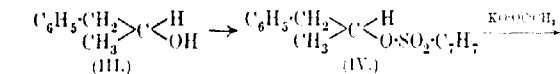
of the mode of reaction of sulphonic esters? Ferns and Lapworth (T., 1912, 101, 273) have shown that the reactions of these esters resemble very closely those of the alkyl haloids.



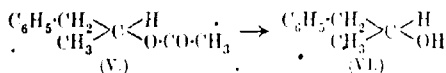
Adopting these views, it is apparent that in reaction I, involving the complete replacement of a group from the asymmetric carbon atom, change of configuration is possible, but in reaction II, in which bonds of the asymmetric carbon atom remain undisturbed, it is unlikely. This is in agreement with the results obtained.

On examination of the magnitudes of the rotations of the ethyl ethers of benzylmethylecarbinol obtained by the three separate methods another important conclusion can be drawn. The "abnormal" reaction occurs with almost complete configurative change. The rotatory power of the ether prepared from the potassium derivative of the alcohol and ethyl bromide is higher than that of the ether prepared by the other two methods, in which a loss in rotatory power might be suspected.

It was decided to extend the investigation and endeavour to prepare a compound from *d*-benzylmethylecarbinyl *p*-toluenesulphonate with complete change of configuration. For such a purpose the compound should be one from which the alcohol could be recovered by methods not likely to cause racemisation or configurative change, so that the rotation of the recovered alcohol could be compared with that of the original. It was found that such compounds, for example, benzylmethylecarbinyl esters of carboxylic acids, could be readily prepared by the interaction of the potassium salts of these acids and the *p*-toluenesulphonate in alcoholic solution. Levorotatory benzylmethylecarbinyl acetate was prepared from pure *d*-benzylmethylecarbinol by the following cycle of reactions:



$[\alpha]_{\text{D}}^{25} = 33.02$ (for 100 mm.), $[\alpha]_{\text{D}}^{25} = 31.11$ (in benzene solution).



$[\alpha]_{\text{D}}^{25} = 7.06$ (for 100 mm.), $[\alpha]_{\text{D}}^{25} = 82.18$ (for 100 mm.).

* Or sodium ethoxide.

The esters derived from *d*-benzylmethylecarbinol and the normal aliphatic acids have been prepared and their optical properties fully described in Part VIII of these investigations (T., 1914, 105, 2261). The acetate prepared from the *d*-alcohol by the action of acetic anhydride is dextrorotatory ($\alpha_{D_{589}}^{20} + 7.13^\circ$ *) and on hydrolysis with alcoholic sodium hydroxide yields the *d*-alcohol of unchanged rotatory power. That both these reactions should be accompanied by *complete* configurative change is unlikely and hence it may be assumed that dextrorotatory benzylmethylecarbinyl acetate has the same configuration as the dextrorotatory alcohol. In the above cycle of reactions, however, this ester is obtained with a levorotation from a dextrorotatory sulphonate, the configuration of which can be said to be dextro.

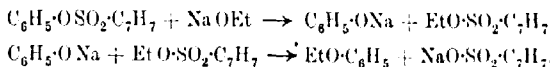
The passage from IV to V therefore occurs by a definitely abnormal reaction, and the almost complete inversion of configuration is clearly demonstrated by these reactions.

The *l*-ethyl ether of benzylmethylecarbinol was also formed during the preparation of the acetate, being produced by the interaction of the *d*-sulphonate and ethyl alcohol, used as the reaction medium, in the presence of potassium acetate. It had $\alpha_{D_{589}}^{21} - 21.92^\circ$, being higher in rotation than that prepared previously. Its presence necessitated very careful fractional distillation of the product, since the boiling points of the acetate and of the ethyl ether are fairly close.

To ensure that the ester obtained was uncontaminated with this ether, a further series of reactions was undertaken in which the *n*-valerate was substituted for the corresponding acetate.

In these reactions, a specimen of *l*-benzylmethylecarbinol with $\alpha_{D_{589}}^{21} - 24.94^\circ$ was converted through the corresponding sulphonate into the *n*-valerate, which had $\alpha_{D_{589}}^{16.5} + 9.76^\circ$ and gave when hydrolysed a *d*-alcohol with $\alpha_{D_{589}}^{20} + 23.98^\circ$. Again the loss in rotatory power was small and complete confirmation of the other reaction was thus obtained.

Ferns and Lapworth (*loc. cit.*) also raise another point which is of interest. Discussing the reaction which occurs between phenyl *p*-toluenesulphonate and sodium ethoxide, they point out that in this case it must be regarded as occurring in two stages:



The reasons they advance are first that the reaction proceeds readily, a fact which does not seem to indicate the breakage of

* All observed rotations recorded in this paper are for 100 mm.

be identical reactions, the phenyl ether of the alcohol being produced during each experiment with inversion¹ of configuration, and therefore the sign of rotation of the ethers obtained should be the same.²

Should, however, the explanation be incorrect, that is, should phenyl *p*-toluenesulphonate react in the same manner as ethyl *p*-toluenesulphonate, it would, when treated with the potassium derivative of the *l*-alcohol, produce a phenyl ether *without* configurative change; and there would result in the two experiments outlined above phenyl ethers of *opposite sign*.

Experimentally it was found that whether the reaction was commenced as indicated in A, or, its course being anticipated, as in B,* the phenyl ethers produced had the same sign of rotation, both being dextrorotatory.

If, therefore, the assumption is made that potassium phenoxide and sodium ethoxide react in the same manner with the *l*-sulphonate, these two experiments give considerable support to the view of the mode of reaction of phenyl *p*-toluenesulphonate put forward by Ferns and Lapworth.

Discussion of Results.

McKenzie and Clough (T., 1913, **103**, 687), by effecting the interconversion of the optically active phenylmethylcarbinols, showed for the first time that the phenomenon of the Walden inversion was not confined to compounds containing a carboxyl or carboalkyloxy-group. Research on the Walden inversion has, however, been mainly confined to carboxylic acids containing also an amino- or a hydroxy-group, or a halogen atom. During the reactions of these compounds involving the complete removal of a group attached to the asymmetric carbon atom a certain amount of "displacement" racemisation (Senter, Drew, and Martin, T., 1918, **113**, 156) occurs. The compounds are also liable in some cases to undergo "catalytic" racemisation, which renders their isolation and purification without loss of rotatory power difficult. When, therefore, the optical enantiomorph of such compounds is obtained after two displacement reactions, a determination of its rotatory power does not truly indicate to what extent the "abnormal" reaction predominates.

If, however, the series of reactions described in the interconversion of the enantiomorphously related benzylmethylcarbinols be examined, it will be seen that, throughout, the compounds involved are stable both as regards their chemical and their optical pro-

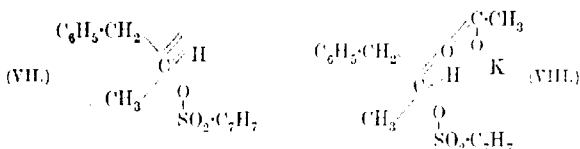
* Using, however, sodium phenoxide instead of potassium phenoxide.

perties. They are compounds which can withstand without catalytic racemisation the experimental conditions to which they are subjected, and also at one stage only (the interaction between the *d*-sulphonate and potassium acetate) is any displacement racemisation likely to occur.

To this fact is partly due the observed completeness of inversion, and, moreover, it points to the stage at which the "abnormal" reaction occurs as the source of the very slight decrease in rotatory power, which is approximately 2 per cent.

This decrease is so small that it must be carefully borne in mind during any attempt to explain the mechanism of this particular reaction. The tendency for the reaction to occur in a definite manner accompanied by inversion of configuration is obviously overwhelming. In other words, it can be said that the group entering the asymmetric molecule is compelled to occupy only one position relative to the other three, and this is a position which entails configurative change.

This position, it seems possible to assume, corresponds to a portion of the surface of the asymmetric carbon atom which is potentially unsaturated. An examination of the constitutional formula (VII), together with a knowledge of the fact that the sulphonic ester exhibits a strong tendency to lose the elements of the corresponding sulphonic acid, enables this possibility to be visualised.

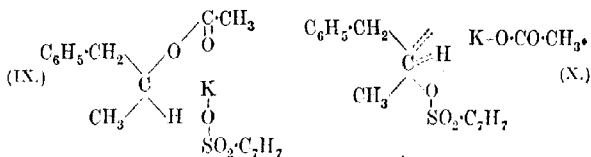


It is postulated that under certain conditions, such as increase of temperature, the sulphonic ester molecule assumes an active condition, arising through the weakening of the attachment of the α -hydrogen atom to the asymmetric carbon atom: this weakening being due to the ester oxygen atom of the $\text{O}\cdot\text{SO}_2\cdot\text{C}_7\text{H}_7$ group exerting its residual valencies.

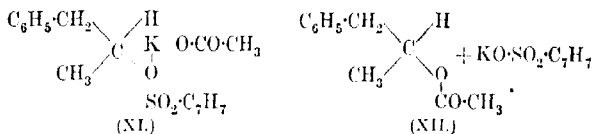
The ester molecule, then, in its active condition contains a hydrogen atom held partly by the residual valencies of the ester oxygen atom and partly by the valency of the asymmetric carbon atom. Thus the portion of the latter atom to which the hydrogen is now but loosely linked is in possession of residual valency. It is postulated that, in an alcoholic solution of potassium acetate, an indirect "abnormal" reaction takes place by the addition of

a molecule of potassium acetate to this unsaturated portion through the agency of the carbonyl oxygen atom which it contains (VIII).

The α -hydrogen atom is displaced by the potassium and the acetyl group usurps the whole affinity of the portion of the asymmetric carbon atom to which it was previously only loosely attached. The potassium *p*-toluenesulphonate formed during this displacement leaves the molecule, the hydrogen liberated during its formation occupying the position thus vacated (IX).



It is suggested also that a direct reaction can occur to an extent sufficient to account for the observed loss of rotatory power. Commencing as before with the molecule of the sulphonic ester in an active condition, it is assumed that it is approached by a molecule of potassium acetate, possibly in an ionised condition (X). No addition occurs at the unsaturated portion of the surface of the asymmetric carbon atom, but instead, the potassium atom displaces the α -hydrogen atom, which assumes its normal state and position in the molecule (XI).

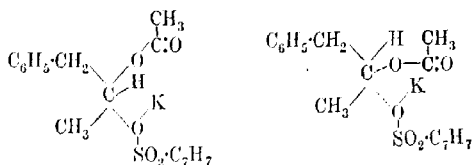


Potassium *p*-toluenesulphonate is then eliminated from the molecule, leaving the acetyl group to enter the position vacated by the group $\text{O}\cdot\text{SO}_2\cdot\text{C}_7\text{H}_7$ (XII).

This would leave an acetic ester of the same configuration as the original sulphonic ester.

In each of these hypothetical molecular interactions the formation of potassium *p*-toluenesulphonate in the complex and its subsequent departure do not necessarily imply that only three valencies of the asymmetric carbon atom are utilised at any particular instant. This salt, when formed, can still remain momentarily attached by the residual valencies of the ester oxygen, and moreover the portion of the asymmetric carbon atom by which it is thus loosely held would be in a partly unsaturated condition.

It would therefore be likely that the atom or group set free through the formation of potassium *p*-toluenesulphonate would be attracted to this position. The arrangement within the bi-molecular complexes before final disruption occurs can therefore be represented as follows :



It is conceivable that a certain proportion of such molecular interactions may miscarry at one or other of the stages through which, it is suggested, they pass, and in such cases an unsaturated hydrocarbon will result.

Experimental evidence of the formation of varying amounts of an unsaturated hydrocarbon has been obtained; in attempting to prepare the ethyl ether of benzylmethylecarbinol from the corresponding sulphonate, if sodium ethoxide be used instead of potassium carbonate, the product consists almost entirely of such a compound, this being due presumably to the too rapid withdrawal of the elements of the sulphonic acid from the molecule.

It will be noticed also that the explanation of these reactions depends on the presence in the ester molecule of a detachable hydrogen atom linked to the same carbon atom as the $\text{O}\text{---}\text{SO}_2\text{C}_7\text{H}_7$ group.

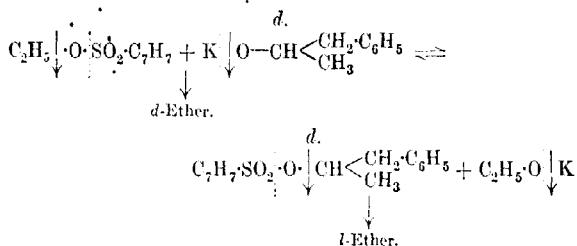
From these assumptions it would follow that ethyl *p*-toluenesulphonate, $\text{CH}_3\text{---CH}_2\text{---O}\text{---}\text{SO}_2\text{C}_7\text{H}_7$, should react readily with potassium acetate in alcoholic solution, whilst phenyl *p*-toluenesulphonate, $\text{C}_6\text{H}_5\text{---O}\text{---}\text{SO}_2\text{C}_7\text{H}_7$, should only react with difficulty, if at all. This conclusion is completely borne out by experiment.

An explanation is still required to account for the slight loss of rotatory power observed during the reactions involved in the preparation of the ethyl ethers.

In this connexion it is noteworthy that the loss of rotatory power is the same, whether these compounds are prepared through the agency of the sulphonic ester of the optically active alcohol, or of ethyl *p*-toluenesulphonate. This case therefore permits of a different explanation from that advanced in the case of the esters.

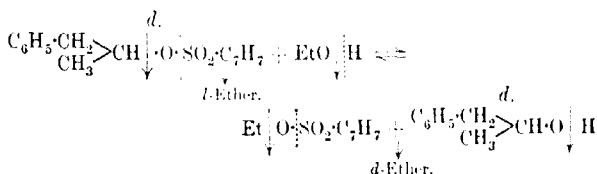
Bearing in mind the supposed anomalous behaviour of phenyl *p*-toluenesulphonate (p. 49), it is postulated that, in the reaction between ethyl *p*-toluenesulphonate and the potassium derivative of

benzylmethylecarbinol, there is a tendency for an exchange of radicals to occur:



The sulphonic ester exercises its ability to decompose with breakage of an O-S linking and the exchange occurs as indicated by the dotted lines. That the amount of interchange would be small is accounted for by the ease with which ethyl *p*-toluenesulphonate reacts with the potassium derivative of the alcohol and hence the rapidity with which the *d*-ether is produced. The yield of *l*-ethyl ether from the right-hand side of the equation will necessarily be small, but since the "abnormal" reaction results in a product of almost full activity, the amount produced need not be large to cause the small loss of rotatory power observed.

This explanation is presumed to be equally applicable to the interaction of *d*-benzylmethylecarbiny *p*-toluenesulphonate and ethyl alcohol in the presence of potassium carbonate.

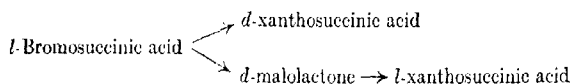


In the above formulæ the dotted lines indicate the method of exchange and the arrows the double decomposition.

Again, it is evident that the extent to which reaction takes place between substances on the right-hand side of the scheme will not be large under the conditions of the experiment. It is significant, however, that if the reaction is carried out in the presence of potassium acetate, which would react with any ethyl *p*-toluenesulphonate formed, the product has a higher rotation, that is, less *d*-ether is produced.

It will be seen that these explanations are in accordance with

the view which has been frequently advanced, that a reaction which results in configurational change proceeds indirectly, being preceded by addition, whilst a normal reaction involves direct substitution. That the decrease in rotatory power or racemisation which accompanies reactions in which the phenomenon of Walden inversion is observed is due rather to the simultaneous formation of the product possessing both *d*- and *l*-configurations has also been previously postulated. Holmberg (*Arkiv Kem. Min. Geol.*, 1916, No. 8, 6) has shown that when chlorosuccinic acid is converted into xanthosuccinic acid the reaction follows two courses simultaneously:



Similarly, Senter and his collaborators (T., 1915, **107**, 638 *et seq.*) showed that the action of ammonia on halogen-substituted acids yields both *d*- and *l*-amino-acids.

The explanation given of the small loss in rotatory power which accompanies the inversions described is perhaps so far based on meagre evidence. It is evident, however, that the predominance of the reaction which results in inversion of configuration prevents acceptance of the view that it occurs with racemisation. The occurrence of racemisation during a reaction suggests a haphazard interaction between two kinds of molecule. It is inconceivable that such an interaction could result in products of the degree of optical purity obtained.

EXPERIMENTAL.

d-Benzylmethylcarbinyl *p*-Toluenesulphonate. — This was prepared as required by the interaction in the cold of equivalent quantities of the alcohol and *p*-toluenesulphonyl chloride in the presence of pyridine. The reaction was complete after twelve hours. On pouring the reaction mixture into water, the ester crystallised, and after filtration was purified by recrystallisation from glacial acetic acid or ethyl alcohol. It had m. p. 94°. 0.7392 Gram of ester required 0.1007 gram of sodium hydroxide for complete hydrolysis, the theoretical amount being 0.1019 gram.

The following determinations of its optical rotatory power were made. The solutions were prepared by dissolving about one gram of the ester in the solvent and diluting to 20 c.c. The observations were taken in a 2-dm. tube.

Solvent.	Grams of solute.	Observed rotation.			[α] _D		
		λ	λ	λ	λ	λ	λ
Ethyl alcohol ...	0.5364	+1.66°	+1.84°	+3.30°	+30.90°	+34.30°	+61.37°
Benzene	1.0126	2.82	3.15	5.83	27.85	31.11	57.58
Chloroform	1.0136	2.53	3.05	5.47	24.97	30.09	53.98
Carbon disulphide	1.0046	3.09	3.75	6.87	30.76	37.33	68.28
Pyridine	0.9910	2.84	3.46	5.88	28.59	34.91	59.33

Reaction between the Potassium Derivative of d-Benzylmethylcarbinol and Ethyl p-Toluenesulphonate.—Four grams of clean potassium were shaken in hot toluene, the latter, when cold, was replaced by 200 c.c. of dry benzene, and 15 grams of the d-alcohol were added. When dissolution of the potassium, which was hastened by gentle warming, was completed, the mixture was cooled, and 40 grams of molten ethyl *p*-toluenesulphonate were slowly added, a voluminous precipitate forming. When the reaction began to slow down, the mixture was shaken vigorously for twenty-two hours. It was then treated with a solution of sodium hydroxide and distilled with steam. To the benzene extract of the distillate dried with potassium carbonate, 20 grams of phthalic anhydride were added, and the solution was boiled, the benzene being allowed to distil off slowly up a fractionating column. The residue, having been heated for ten hours at 110°, was poured into dilute sodium carbonate solution, and after remaining over-night, this solution was extracted with ether. The benzylmethylcarbinyl ethyl ether obtained from the dried ethereal extract was distilled under reduced pressure, and after three fractionations 9 grams were obtained: b. p. 92–93°/19 mm., d_4^{20} 0.9168, n_D^{20} 1.4848, and α_D^{20} +19.81°.

Reaction between Sodium Ethoxide and Benzylmethylcarbinyl p-Toluenesulphonate.—The most successful experiment of this series was conducted as follows: Twenty grams of the sulphonic ester (prepared from a sample of partly active alcohol with α_D^{20} –7.82° and having $[\alpha]_D^{20}$ –6.92° in benzene) were dissolved in 100 c.c. of anhydrous ethyl alcohol, and while the solution was being warmed on a water-bath a solution of 2 grams of sodium in 50 c.c. of alcohol was added during three and a half hours. The alcohol was then distilled off through a column, the residue poured into water, and the oily layer which formed extracted with ether. The product obtained from the dried ethereal extract was repeatedly distilled and gave two main fractions.

Fraction A, b. p. 62–65°/14 mm., amounted to 3 grams. It was optically inactive after four redistillations. It rapidly decolorised bromine water, had n_D^{20} 1.5331, d_4^{20} 0.9045, and was an unsaturated hydrocarbon.

Fraction B, b. p. 85–88°/14 mm., closely resembled the ethyl ether of benzylmethylcarbinol. About 1.5 grams were obtained having $\alpha_{D,20}^{25} + 4.12^\circ$.

Reaction between d-Benzylmethylcarbinyl p-Toluenesulphonate and Ethyl Alcohol in the presence of Potassium Carbonate.—A mixture of 20 grams of the *d*-sulphonic ester, prepared from the pure *d*-alcohol, 150 c.c. of absolute alcohol, and 20 grams of dry, finely powdered potassium carbonate was heated under reflux for thirty-seven hours. The alcohol was then distilled off and the residue poured into water. The oil which separated was extracted with ether. Since benzylmethylcarbinol might have been formed during the reaction by hydrolysis of the sulphonic ester, the product was heated with phthalic anhydride for ten hours at 100–110° and poured into sodium carbonate solution, from which the required product was isolated in the usual way by extraction with ether. On distillation a very small quantity of a hydrocarbon was isolated. The main fraction, 6.9 grams, boiled at 85–100°/20 mm. After two distillations, the mixed ether (5 grams) had b. p. 92–94°/20 mm., $d_4^{25} 0.9177$, $n_D^{25} 1.4878$, and $\alpha_{D,20}^{25} - 19.90^\circ$, which was unchanged by subsequent distillation.

Reaction between d-Benzylmethylcarbinyl p-Toluenesulphonate and Potassium Acetate.—Thirty grams of the pure *d*-ester were dissolved in 150 c.c. of absolute alcohol, and 21 grams of freshly fused potassium acetate were added. The clear solution obtained on warming soon became clouded by a gelatinous precipitate, which rapidly changed to white, crystalline plates. After six hours' heating under reflux, the alcohol was distilled off and the residue poured into water. The oil which separated was isolated with ether in the usual manner.

On distillation, a small fraction, b. p. below 100°/16 mm., was obtained, the main fraction, 14.8 grams, boiling at 100–113°/16 mm. After three fractionations, 7.8 grams of *l*-benzylmethylcarbinyl acetate, b. p. 112–114°/18 mm., were isolated having $d_4^{25} 0.9978$, $n_D^{25} 1.4881$, and $\alpha_{D,20}^{25} - 7.06^\circ$.

On hydrolysis with sodium hydroxide, 1.0660 grams required 0.2391 gram of NaOH (theory 0.2395 gram).

The remainder of the *l*-acetate was hydrolysed in alcoholic solution. The regenerated *l*-benzylmethylcarbinol had b. p. 108°/21 mm., and $\alpha_{D,20}^{25} - 32.48^\circ$, whereas the *d*-alcohol used for the preparation of the sulphonate had $\alpha_{D,20}^{25} - 33.02^\circ$.

The lower-boiling portions of the distillate were heated with alcoholic sodium hydroxide and from the product any active alcohol present was removed in the usual way with phthalic anhydride. The product obtained was separated by distillation into two fractions: A, b. p. 78–79°/20 mm., B, b. p. 90–95°/20 mm.

A weighed about 1.5 grams and consisted mainly of an unsaturated hydrocarbon. B_1 when redistilled, had b. p. $93^\circ/19$ mm., $n_{D_{20}}^{25}$ 1.4909, d_4^{25} 0.9230, and $\alpha_{D_{40}}^{21}$ -10.96° in a 50-mm. tube. Its refractive index and density are thus both somewhat higher than those obtained for the ethyl ether of benzylmethylcarbinol by the other methods.

This experiment was repeated using a partly active alcohol ($\alpha_{D_{40}}^{21}$ -7.82°), which gave a *p*-toluenesulphonate having $[\alpha]_{D_{40}}^{21}$ -6.92° in benzene solution. Twenty grams of this ester, dissolved in 120 c.c. of alcohol, were heated under reflux with 14 grams of potassium acetate; 3.8 grams of benzylmethylcarbinyl acetate were isolated, b. p. $107^\circ/14$ mm., d_4^{25} 0.9968, $n_{D_{20}}^{25}$ 1.4897, and $\alpha_{D_{40}}^{25}$ $+2.0^\circ$. On hydrolysis it yielded a benzylmethylcarbinol having $\alpha_{D_{40}}^{25}$ $+7.44^\circ$.

Other products of the reaction were a hydrocarbon and the ethyl ether of benzylmethylcarbinol, which were not completely isolated owing to the small bulk of the mixture.

Reaction between Benzylmethylcarbinyl p-Toluenesulphonate and Potassium Acetate when dissolved in Glacial Acetic Acid.—Nineteen grams of the sulphonate ($[\alpha]_{D_{40}}^{21}$ -6.92° in benzene solution), prepared from an alcohol having $\alpha_{D_{40}}^{21}$ -7.82° , were dissolved in 100 c.c. of glacial acetic acid. The mixture was warmed for twenty-four hours on a water-bath and remained quite clear. It was poured into water, the acid neutralised with sodium carbonate, and the solution extracted with ether. The product obtained from the ethereal extract was carefully fractionated. After three distillations, 5.7 grams of benzylmethylcarbinyl acetate were obtained which had d_4^{25} 0.9961, $n_{D_{20}}^{25}$ 1.4896, and $\alpha_{D_{40}}^{25}$ $+1.06^\circ$. This on hydrolysis gave an alcohol having $\alpha_{D_{40}}^{25}$ $+3.74^\circ$, n_D^{25} 1.5214, and d_4^{25} 0.9879.

Reaction between Benzylmethylcarbinyl p-Toluenesulphonate and Potassium n-Valerate.—Potassium *n*-valerate was prepared by neutralising *n*-valeric acid with the theoretical quantity of potassium carbonate dissolved in the minimum of water, and evaporating the mixture to dryness. Forty grams of the residue were dissolved in 182 grams of absolute alcohol and 90 grams of benzene, and the solution dried by distillation until the temperature was 78.3° . Thirty grams of the sulphonate prepared from benzylmethylcarbinol ($\alpha_{D_{40}}^{21}$ -24.94°) were added to the alcoholic solution, and the mixture was heated under reflux for six hours. On isolation of the product as described in previous experiments, 9.5 grams of benzylmethylcarbinyl *n*-valerate were obtained, b. p. $147-148/19$ mm., d_4^{25} 0.9605, $n_{D_{20}}^{25}$ 1.4817, and $\alpha_{D_{40}}^{25}$ $+9.76^\circ$. On hydrolysis, it gave an alcohol having $\alpha_{D_{40}}^{25}$ $+23.98^\circ$.

During this reaction also, the lower fractions obtained were small in bulk and consisted largely of benzylmethylecarbinyl ethyl ether.

Reaction between Sodium Phenoxide and Benzylmethylecarbinyl p-Toluenesulphonate.—To a solution of sodium phenoxide in absolute alcohol prepared from 5.6 grams of phenol and 1.35 grams of sodium, 17 grams of benzylmethylecarbinyl *p*-toluenesulphonate, prepared from a partly active alcohol ($\alpha_{D}^{20} = 6.44^\circ$), were added, and the mixture was heated under reflux for four hours. The alcohol was distilled off, the residue poured into a dilute solution of sodium hydroxide, and after extraction with ether, fractional distillation of the product gave two main fractions: (1) an unsaturated substance, about 2 grams, b. p. $68-70^\circ/14$ mm.; (2) benzylmethylecarbinyl phenyl ether, 4 grams, b. p. $156-157^\circ/14$ mm., $\alpha_{D}^{20} + 14.12^\circ$, d_4^{20} 1.0288, n_D^{20} 1.5573, and $[R]_{D}^{20}$ 66.40 (calc. 65.91).

Reaction between Phenyl p-Toluenesulphonate and the Potassium Derivative of Benzylmethylecarbinol.—Twelve grams of partly active alcohol ($\alpha_{D}^{20} = 6.44^\circ$) were added to 120 c.c. of dried benzene, in which were suspended 3 grams of finely divided potassium. When all the metal had dissolved, a benzene solution of 20 grams of phenyl *p*-toluenesulphonate was added. The solution remained clear for some time, then a voluminous precipitate suddenly formed. The mixture, having been heated under reflux for five hours, and sodium hydroxide added, was distilled with steam. The distillate was extracted with benzene, and the residue from the dried benzene extract distilled. Three fractions were obtained: A, b. p. $70-80^\circ/17$ mm. (less than 1 gram). B, b. p. $103-17$ mm. (7 grams). C, b. p. $157-160^\circ/17$ mm. (1.5 grams).

A appeared to be identical with the hydrocarbon previously obtained. B was benzylmethylecarbinol having $\alpha_{D}^{20} = 4.36^\circ$, whilst C was similar to the phenyl ether obtained in the previous experiment and had $\alpha_{D}^{20} + 10.20^\circ$.

Although the sign of rotation of this ether is definite, the magnitude of the rotation is not above suspicion, since the small amount obtained made efficient purification difficult.

The author desires to express his thanks to Dr. R. H. Pickard, F.R.S., and Dr. J. Kenyon for their guidance during the course of this research, and to acknowledge the receipt of a personal grant from the Department of Scientific and Industrial Research. The materials used were purchased in part with a grant made by the Government Grant Committee of the Royal Society.

VI.—Nitration of 3-Chloroacenaphthene.

By GLADYS FARNELL.

IN the nitration of 3-chloroacenaphthene, described below, a uniform product was not obtained, and it can be shown that the nitro-group has taken up alternative positions. 3-Chloro-4-nitroacenaphthene, m. p. $136-138^{\circ}$, was isolated, and its constitution proved. A second product, not entirely uniform and melting at $160-166^{\circ}$, was obtained, and this also appears to be a mononitro-derivative of chloroacenaphthene.

Nitration.—Twenty grams of 3-chloroacenaphthene, m. p. 69° , prepared by Crompton and Walker's method (T., 1912, **101**, 958) and purified by distillation and crystallisation from alcohol, were dissolved in the minimum quantity of glacial acetic acid, and 4.4 c.c. of nitric acid (d 1.5) so added, with vigorous shaking, that no appreciable temperature change occurred. The liquid, which changed from yellow to red, deposited crystals, long, pale yellow needles after three hours and, later, spherical clusters. By repeated crystallisation from alcohol, it was possible to isolate from the crude product the two compounds already mentioned, melting at $160-166^{\circ}$ and $136-138^{\circ}$, respectively, which are formed in about equal quantity. The final yield of the latter was only 10 per cent. of the theoretical; attempts to improve the yield by varying the conditions of the nitration were not successful [Found: N = 6.07, 6.06; Cl, by the lime method, = 15.23, 15.08, by Rosenmund's method (Ber., 1918, **51**, 578), = 15.30. $C_{12}H_8O_2NCl$ requires N = 6.02; Cl = 15.20 per cent.].

The results indicate that the compound is a mononitrochloroacenaphthene. A study of its reduction products served to establish its constitution.

Reduction.—The chloronitroacenaphthene was first reduced with sodium hyposulphite by Sachs and Mosbach's method (Ber., 1911, **44**, 2855). The product after purification by crystallisation from hot water was colourless and melted at 145° (Found: Cl, by Rosenmund's method, = 16.89. $C_{12}H_8NCl$ requires Cl = 17.45 per cent.).

Chloroaminoacenaphthene crystallises in fine, colourless needles from water, alcohol, or alcohol-water mixtures. It darkens on heating or on exposure to light. Its solutions are coloured blue by ferric chloride, and, in the presence of acid, give a green precipitate with sodium nitrite. In these points it closely resembles the ordinary aminoacenaphthene, in which, as shown by Graebe (Annalen, 1903, **327**, 81), the amino-group is in the position 3

(or 4). This analogous behaviour suggested that the amino-groups in the two compounds are in similar positions, which could only be the case if the nitro-group had originally entered 3-chloroacacenaphthene in the position 4. Were this so, the replacement of the chlorine of the above chloroaminoacacenaphthene by hydrogen should yield the familiar 3-aminoacacenaphthene.

Such a replacement occurs in the reduction with hydrogen described above, but a simpler method of arriving at the same result was discovered in the direct reduction of the original chloro-nitroacacenaphthene. This compound was reduced with hydrogen in the presence of palladium. It was found that, in addition to the removal of the chlorine, the nitro-group was reduced to an amino-group. When purified, the amino-compound thus obtained resembled 3-aminoacacenaphthene perfectly in its appearance and behaviour. It melted at 107° , alone or mixed with this substance, and gave the colour reactions with ferric chloride and sodium nitrite already described. It is therefore the aminoacacenaphthene of known constitution, with the amino-group in the position 3 (or 4). The production of this compound by the direct reduction of the chloronitroacacenaphthene, melting at $136-138^{\circ}$, in which chlorine is in the position 3, proves that the nitro-group is in the position 4.

On oxidation with chromic acid, it gives the corresponding *chloronitronaphthalic acid*. This was obtained as a yellow powder, and, on crystallisation from glacial acetic acid, it gave pale yellow, shining leaflets of the *anhydride* (Found: N = 4.69. $C_{12}H_4O_5NCl$ requires N = 5.04 per cent.). Sodium, calcium, and barium salts were prepared, and the calcium salt was analysed (Found: Ca = 11.76, 11.69. $C_{12}H_4O_5NClCa$ requires Ca = 11.99 per cent.).

The compound melting at $160-166^{\circ}$, formed along with the above chloronitroacacenaphthene in the nitration of 3-chloroacacenaphthene, was not obtained in sufficient quantity in a pure state for its complete examination. It was found to contain 6.04 per cent. of nitrogen, and therefore is probably also a mononitrochloroacacenaphthene, or a mixture of such compounds.

This work was suggested to me by Mr. H. Crompton, and I am indebted to him for guidance in carrying it out.

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[Received, November 6th, 1922.]

VII.—*The Chemistry of the Glutaconic Acids.*
 Part XIII. *The Isomerism due to Retarded Mobility.*

By JOCELYN FIELD THORPE and ARTHUR SAMUEL WOOD.

EARLY this year, Feist (*Annalen*, 1922, 428, 25) published a theoretical discussion of the evidence which has accumulated during the past seventeen years regarding the structure of the glutaconic acids and reached the general conclusion that the isomerism of these acids is of the "ordinary" geometrical type and that the adoption of a symmetrical formula for glutaconic acid is unnecessary. He supports his conclusion by some further experimental work embodied in three papers (with Breuer, *ibid.*, 59, 68; and with Breuer and Lubricht, *ibid.*, 40), in two of which he deals with the products formed by the decomposition of the ozonides of certain acids of the series, and; in the third, with the question of the existence of the three isomerides of β -phenyl- α -methylglutaconic acid isolated by us (T., 1913, 103, 1574).

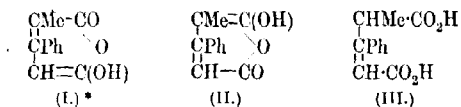
Feist gives an excellent summary of the experimental facts which have led to the conclusion that the formulae of glutaconic acid, and those of its derivatives which contain a mobile hydrogen atom, must differ from those of the ordinary unsaturated dicarboxylic acids in some fundamental manner, but, unfortunately, he does not criticise these facts or their theoretical bearing in detail, and therefore it is difficult to follow his general reasoning. Nevertheless, it would seem that our views and his are not, in reality, very different, because when he says that "the absence of a second form of glutaconic acid is readily explicable on the assumption that the double bond changes position," he can only mean that the absence of isomerism is due to symmetry, because it is obvious that any movement of the double bond in glutaconic acid will produce—as does the movement of the double bonds in either of the Kekulé benzene individuals—a substance having an identical space formula. It is true that he guards himself by the alternative "oder ausschliesslich die stabilere *trans*-modifikation bilden wird," but, of course, this cannot be the case, because the only known form of glutaconic acid is a *cis*-form, that is, it readily passes into the anhydride, a behaviour which is quite different from that of the known *trans*-forms of the series, such as *trans*- $\alpha\alpha$ -dimethylglutaconic acid or *trans*- $\alpha\alpha$ -trimethylglutaconic acid, which do not form anhydrides, or, for the matter of that, of the *trans*-modification of β -phenyl- α -methylglutaconic acid, which he himself mentions in his paper.

In his ozone experiments, Feist prepares the ozonides of the two

forms of $\alpha\beta$ -dimethylglutaconic acid and of his two forms of β -phenyl- α -methylglutaconic acid and studies the products obtained from them on degradation. If, however, such evidence were accepted as proof of structure, the formula of benzene would have been settled when Harries carried out his classical researches on the formation and degradation of its ozonide. Still, the experiments described by Feist are instructive, because they show that the ozonides from both the "cis" and "trans" forms of ethyl β -phenyl- α -methylglutaconate yield the same four products and that two pairs of these are those which would normally have been derived from two esters having the formulae $\text{CO}_2\text{Et}\cdot\text{CH}_2\cdot\text{CPh}\cdot\text{CHMe}\cdot\text{CO}_2\text{Et}$ and $\text{CO}_2\text{Et}\cdot\text{CH}\cdot\text{CPh}\cdot\text{CHMe}\cdot\text{CO}_2\text{Et}$, respectively. In other words, the behaviour towards ozone is exactly that which one would expect if the esters had reacted in the "normal" form. Finally, Feist has succeeded in isolating only two forms of β -phenyl- α -methylglutaconic acid. One of these is the *trans*-labile modification (m. p. 155°) described by us (*loc. cit.*). The other melts at 151° and is evidently a *cis*-acid, because it is readily converted into an anhydride (m. p. 94°). The two other acids of this formula prepared by us were the "normal" acid (m. p. 120°) and the *cis*-labile acid (m. p. 108°). Feist considers that these two acids are impure specimens of his acid (m. p. 151°), and attempts to prove his point by determining the melting points of varying mixtures of the *trans*-labile acid (m. p. 155°) and his *cis*-acid (m. p. 151°). As our acids were made by the hydration of the pure anhydride, it is not possible for them to have contained any of the *trans*-modification. Moreover, our acids were pure compounds and the repeated recrystallisation of specimens which remained in our possession has failed to alter the melting points given above. The explanation of the discrepancy in our results and those of Feist without doubt rests on the fact that the anhydride (hydroxy-anhydride) prepared by Feist from his acid melting at 151° is a different substance from that prepared by us from the acids melting at 120° and 108°, respectively. The two anhydrides melt at much the same temperature, but they react very differently on hydration, and although we have not succeeded in isolating the pure anhydride prepared by Feist, we have been able to show that our anhydride is, at any rate partly, converted into Feist's anhydride when it is distilled under diminished pressure. This follows, because a specimen of our anhydride which before distillation gave, on hydration, the acids melting at 120° and 108° as sole products, yielded, after distillation, a mixture of acids from which we were able to isolate a small quantity of Feist's *cis*-acid melting at 151°.

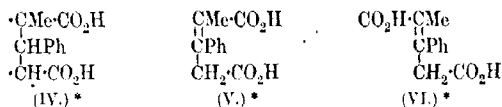
It is evident, therefore, that in a glutaconic system such as that

which is contained in the molecule of β -phenyl- α -methylglutaconic acid, the mobility of the hydrogen atom is so far decreased as to render possible the isolation of two forms of the hydroxy-anhydride which can be represented by the formulæ I and II.



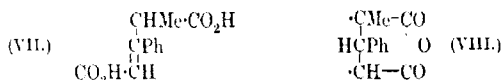
M. p. 94° (T. and W.). M. p. 93–94° (F.). *cis*-acid, m. p. 151° (F.).

The hydroxy-anhydride (II) gives, on hydration, Feist's acid (III), and the hydroxy-anhydride (I) a mixture of the "normal" acid (IV) and the *cis*-labile acid (V); the *trans*-acid being represented by (VI).



M. p. 120° (T. and W.). M. p. 108° (T. and W.). M. p. 155° (T. and W., F.).

Two other compounds of this formula should also be capable of isolation, namely, the *trans*-acid (VII) corresponding with Feist's *cis*-acid (III), and the "normal" anhydride (VIII),



but we have not as yet been able to isolate these substances.

From these experiments it would appear, therefore, that a glutaconic acid, in which the presence of groups in the three-carbon system so far retards the movement of the tautomeric hydrogen atom as to enable it to remain within either the three-carbon system or one or other of the systems C-C-O, can be isolated in five forms—two *trans*-, two *cis*-, and one "normal."

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[Received, December 1st, 1922.]

* The structures of the compounds marked * are, we consider, fixed by the fact that the three acids IV, V, and VI give *isobutenylbenzene*, CHMe:CPh-CH₂, when they are boiled with dilute mineral acid (compare Thorpe and Wood, *loc. cit.*, p. 1572).

VIII.—*The Higher Oxide of Cobalt.*

By OWEN RHYS HOWELL.

THE precipitation of a higher oxide of cobalt from solution by means of alkali and an oxidising agent has received considerable attention (Bayley, *Chem. News*, 1879, **39**, 81; Carnot, *Compt. rend.*, 1889, **108**, 610; Schröder, *Chem. Zentr.*, 1890, i, 931; Vortmann, *Ber.*, 1891, **24**, 2744; McLeod, *Rep. Brit. Assoc.*, 1892, 669; Mawrow, *Z. anorg. Chem.*, 1900, **24**, 263; Hüttner, *ibid.*, 1901, **27**, 81; Metzl, *ibid.*, 1914, **86**, 358), but the nature of the oxide does not appear to have been satisfactorily established. An attempt was therefore made to throw light on the subject by a quantitative examination of the precipitates formed by the action of alkaline hypochlorites on cobalt sulphate. In one series of experiments, the cobalt salt was precipitated with sodium hydroxide and sodium hypochlorite; in a second series, lime and bleaching powder were used.

EXPERIMENTAL.

Materials.—The cobalt sulphate was free from nickel and contained only a trace of iron. The sodium hypochlorite was made by passing washed chlorine into aqueous sodium hydroxide below 15° until chlorination was almost complete, a little free alkali being left to retard decomposition of the hypochlorite. The calcium hypochlorite was prepared by extracting bleaching powder with water.

Method of Investigation.—A solution containing 15 grams of cobalt sulphate in 100 c.c. of water was precipitated with the requisite amount of alkali and hypochlorite dissolved in 500 c.c. of water, after determining accurately the concentration of the hypochlorite (by liberation of iodine) and of the alkali (by adding hydrogen peroxide to remove the hypochlorite and then titrating, due allowance being made for the acidity of the hydrogen peroxide). The mixture was stirred for two hours, during which any excess of hypochlorite was decomposed by the catalytic action of the oxide. The precipitate was allowed to settle over-night, filtered on a Buchner funnel, washed, collected in a porcelain dish, and weighed. For analysis, samples of about 2 grams were weighed in small tubes, and dropped into a solution of potassium iodide acidified with hydrochloric acid; the liberated iodine was titrated and the available oxygen calculated.

In later experiments, the suspended precipitate was titrated immediately after the completion of the decomposition of the

hypochlorite without waiting for it to settle. In this way it was established that the oxide, once formed, is quite stable, since the same value was found for the available oxygen immediately after precipitation and after the precipitate had been kept for some weeks.

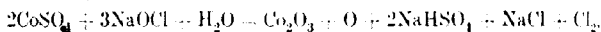
Action of Hypochlorite Alone.—The following results were obtained with sodium hypochlorite free from alkali:

TABLE I.
Equivalents of available oxygen in the precipitate.

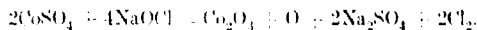
Equivalents of NaOCl.	Per equivalent of Co taken.	Per equivalent of Co precipitated.
0.776	0.471	1.050
1.400	0.700	1.045
1.960	0.786	1.050
2.494	0.834	1.056
3.576	0.885	1.048
4.988	0.934	1.053

The amount of available oxygen was estimated as described above and the amount of cobalt in the precipitate was also estimated in each case by taking an aliquot part of the suspension of the oxide, filtering, washing, and reducing to metal in a stream of hydrogen. The composition of the precipitate is seen to be independent of the amount of hypochlorite used, the proportion of available oxygen being constant at 1.05 equivalents. The direct action of the hypochlorite is therefore to yield the sesquioxide, which would contain 1 equivalent of available oxygen.

The results are shown graphically in Fig. 1, where the amount of available oxygen found in the precipitate is plotted against the total amount taken. The slope of the curve indicates that the reaction proceeds initially according to the equation



the course of which is represented by the tangent (NaOCl:Co₂O₃ 3:1) in Fig. 1 (A); but as the amount of hypochlorite is increased there is probably an increased tendency to produce neutral sodium sulphate, as shown in the equation



Since the composition of the precipitate is constant, its content of available oxygen is a measure of the amount of cobalt precipitated: the ordinates denoting this quantity fall away rapidly from the tangent, showing that a very large excess of hypochlorite would be necessary to secure complete precipitation of the cobalt. This is attributed to the fact that the particles of sesquioxide appear to be coated with a higher oxide which catalytically decomposes

the hypochlorite, an action that is specially rapid in these alkali-free solutions.

Action of Hypochlorite in Presence of Alkali.—A constant excess of alkali was used with varying amounts of hypochlorite. The results obtained with the sodium compounds are given in Table II and those with the calcium compounds in Table III. The values are plotted in Fig. 1 (B).

FIG. 1.

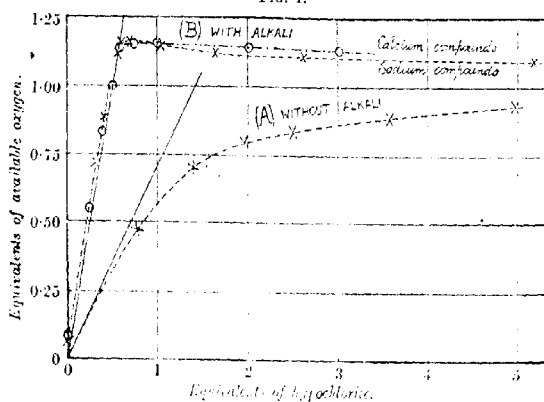


TABLE II.

NaOH.	Na ₂ O ₂ .	Total alkali.	NaOCl.	Available oxygen in the precipitate.
1.469	0.044	1.513	Nil	0.060
1.400	0.022	1.422	0.320	0.712
1.400	0.022	1.422	0.405	0.886
1.421	0.011	1.432	0.502	1.119
1.421	0.022	1.443	0.601	1.155
1.410	0.011	1.421	0.703	1.162
1.341	0.069	1.410	1.051	1.149
1.421	0.022	1.443	1.040	1.121
1.390	0.045	1.435	2.629	1.106
1.406	0.022	1.428	3.192	1.095

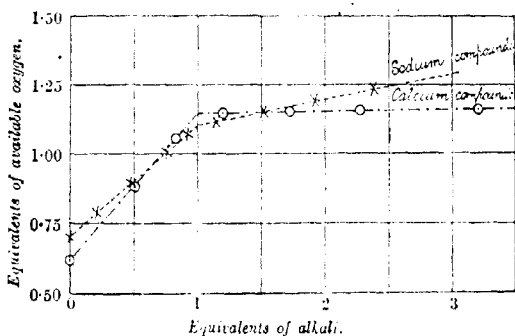
TABLE III.

Ca(OH) ₂ .	Ca(OCl) ₂ .	Available oxygen in the precipitate.	Ca(OH) ₂ + Ca(OCl) ₂ .	Available oxygen in the precipitate.
1.192	Nil	0.084	1.181	0.745
1.192	0.248	0.550	1.192	1.142
1.192	0.396	0.829	1.192	1.150
1.187	0.507	1.000	1.715	1.150
1.204	0.596	1.112		

In every case the quantities are given in equivalents per equivalent of cobalt, the equivalent of a hypochlorite being taken as the quantity which contains 8 grams of available oxygen. Since, in presence of an excess of alkali, precipitation is always complete, the available oxygen calculated on the cobalt taken is the same as on the cobalt precipitated.

It is seen that, owing to atmospheric oxidation of the hydroxide, the precipitate contains more oxygen than that supplied by the hypochlorite so long as the quantity of the latter is less than the quantity (half an equivalent) that is required to oxidise all the hydroxide to sesquioxide. If more than this quantity is added, oxidation again proceeds beyond the stage of sesquioxide, and the peroxide so formed catalytically decomposes the hypochlorite.

FIG. 2.



Since, however, the peroxide appears to be stabilised by the excess of alkali (see p. 69), the action of the hypochlorite proceeds further than when hypochlorite is used alone, the extent depending on the excess of alkali. When still more hypochlorite is used, the available oxygen in the precipitate falls off towards the slightly lower value given by hypochlorite alone.

Action of Alkali.—A constant amount of hypochlorite was used with variable amounts of alkali. The results with the sodium compounds are given in Table IV and those with the calcium compounds in Table V. The values are plotted in Fig. 2. The two curves are not directly comparable because the precipitating solutions were not of the same composition in the two cases.

Both curves exhibit a break at one equivalent of alkali. Up to this point the precipitation of the cobalt is incomplete, since in the absence of alkali a very large excess of hypochlorite is required

TABLE IV.

		Available oxygen in the precipitate calculated on			
NaOH.	Na ₂ CO ₃ .	Total alkali.	NaOCl.	(i) cobalt taken.	(ii) cobalt precipitated.
Nil	Nil	Nil	1.400	0.700	1.050
0.190	0.032	0.222	1.393	0.786	1.059
0.462	0.020	0.482	1.393	0.895	1.072
0.740	0.018	0.758	1.400	1.002	1.075
0.908	0.018	0.926	1.416	1.072	1.089
1.104	0.011	1.115	1.393		1.106
1.502	0.018	1.520	1.393		1.150
1.910	0.011	1.921	1.400		1.184
2.342	0.042	2.384	1.400		1.226
2.910	0.023	2.933	1.400		1.280

TABLE V.

		Available oxygen calculated on	
Ca(OH) ₂ .	Ca(OCl) ₂ .	(i) cobalt taken.	(ii) cobalt precipitated.
0.011	1.143	0.619	1.052
0.512	1.153	0.881	1.097
0.821	1.147	1.055	1.125
1.200	1.153		1.140
1.721	1.153		1.150
2.278	1.153		1.152
3.206	1.143		1.156

to throw down all the cobalt, whereas the precipitation of the cobalt by alkali is quantitative. The figures in the last column show that the precipitate is in every case a slightly peroxidised sesquioxide; the proportion of available oxygen which it contains is, however, not constant, but increases with the amount of alkali that is used. In the case of sodium hydroxide, the increase continues when the alkali is in excess of one equivalent and is even more rapid than when smaller quantities of alkali are being used to precipitate the cobalt. In the case of lime, this secondary increase in presence of an excess of alkali does not take place, since the active mass of the calcium hydroxide is limited by its sparing solubility.

The lowest figures in the last column of Tables IV and V are those given by hypochlorite alone, even when present in large excess. Some additional factor must therefore be introduced to account for the higher degree of oxidation which results from the use of alkali. For this reason, it is suggested (i) that cobalt hydroxide is more readily peroxidised than cobalt sulphate and (ii) that the peroxide thus formed is perhaps hydroxylated, for example, $\text{OH}\cdot\text{Co}\cdot\text{O}\cdot\text{OH}$, and in this form is more stable than cobalt peroxide precipitated directly from solution by sodium hypochlorite.

*Action of Sodium Carbonate.**—A number of experiments have been made in which the cobalt solution was precipitated with a mixture of sodium carbonate and sodium hypochlorite. Under these conditions, an almost black, gelatinous precipitate is obtained, and a green solution, which deposits the black substance slowly, but more rapidly on dialysis. The green solution appears to be colloidal and gives the Tyndall cone. The precipitate contains the carbonate radicle in addition to "available" oxygen and appears to be a peroxidised carbonate. This action will be made the subject of further investigation.

Influence of Temperature.—In this series of experiments, the composition of the reacting solutions was the same in each case. Both solutions were warmed to the requisite temperature before mixing and kept at this temperature while stirred for half an hour.

(a) Precipitating solution, NaOH 1.35 equivs. NaOCl 1.35 equivs.

Temp. of precipitation ...	15°	30°	60°	80°	80° †
Available oxygen	1.156	1.175	1.180	1.179	1.181

(b) Precipitating solution, Ca(OH)₂ 1.24 equivs. Ca(OCl)₂ 1.40 equivs.

Temp. of precipitation	15°	30°	42°	60°	80°	70° †
Available oxygen	1.150	1.157	1.161	1.166	1.167	1.157

† After boiling for four hours.

It is evident that the temperature of precipitation has practically no influence on the composition of the precipitate formed. Moreover, the substance is a very stable one, for even after boiling for four hours there was no decrease in the content of oxygen.

Influence of Concentration.—In this series of experiments all conditions were constant except the concentrations of the reacting solutions. In B, the concentration was the same as in all previous experiments; in A, it was half, and in C double, this value.

(a) Precipitating solution, NaOH 1.35 equivs. NaOCl 1.35 equivs.

	A.	B.	C.
Concentration	half	unity	double
Available oxygen	1.150	1.150	1.156

(b) Precipitating solution, Ca(OH)₂ 1.68 equivs. Ca(OCl)₂ 1.46 equivs.

	A.	B.	C.
Concentration	half	unity	double
Available oxygen	1.147	1.150	1.155

* Compare Durrant (P., 1896, **12**, 244) and McConnell and Hanes (T., 1897, **71**, 589), who have examined the precipitation of cobalt solutions by bicarbonates and hypochlorites.

It is evident from these figures that the concentration of the reactants has practically no influence on the composition of the precipitate.

Summary.

1. Hypochlorites free from alkali immediately precipitate from aqueous solutions of cobalt sulphate a slightly peroxidised cobalt sesquioxide of constant composition containing about 1.05 equivalents of available oxygen; but since the peroxide catalytically decomposes the hypochlorite, the precipitation is far from quantitative.

2. When less than half an equivalent of hypochlorite is used with an excess of alkali, more available oxygen is found in the precipitate than was used in the hypochlorite; this is attributed to atmospheric oxidation of the precipitated hydroxide.

3. A higher degree of oxidation is reached with hypochlorite and alkali than with hypochlorite alone. This is attributed to the formation of a hydroxylated peroxide, by direct oxidation of cobaltous hydroxide.

4. The temperature has no important influence on the composition of the precipitate. The oxide is very stable, since it can be kept indefinitely and prolonged boiling causes no loss of available oxygen.

5. The concentration of the reacting solutions likewise has practically no influence on the composition of the precipitate.

The author would express his thanks to Principal B. Mouat Jones and Prof. T. C. James for giving him every facility for carrying out this work, and to Prof. T. M. Lowry for his kindly interest.

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[Received, December 30, 1922.]

IX.—*The Relation between the Crystal Structure and the Constitution of Carbon Compounds. Part I. Compounds of the Type CX_n .*

By ISABEL ELLIE KNAGGS.

CONSIDERING the large number of organic compounds which have been examined crystallographically, it is remarkable that no kind of comprehensive generalisation connecting their crystalline form with their molecular structure appears to have been reached. Yet

it is abundantly clear that a connexion between the two must exist, and no doubt the difficulty which workers have had in interpreting their results is to be traced to the complexity of the relationship.

The extensive investigations which have been carried out in the X-ray analysis of crystals since von Laue's discovery in 1912 of the diffraction of X-rays by crystals have already gone far to solve the problem as regards inorganic compounds. But in organic compounds the structures are essentially more complex and present difficulties in the way of X-ray analysis which it will not be easy to surmount. In the case of aromatic carbon compounds, recent work of Sir William Bragg (*Proc. Physical Soc.*, 1921, **34**, 1) on the X-ray analysis of naphthalene and anthracene has afforded striking evidence of the persistence of the benzene ring in one of its forms and therefore perhaps also of the chemical molecule in the crystalline state. If this should be generally applicable to aromatic compounds, the problem in their case would be considerably simplified.

In the case of the aliphatic compounds, however, no such evidence is yet to hand, and at the present stage of the problem it would appear that it is only as the result of the examination of the crystalline form of the simplest molecular types and the observation of regularities which they present that any progress can be expected. Therefore at the outset of the investigation, of which the present communication constitutes a preliminary part, it is proposed to examine those aliphatic compounds which are simplest in molecular structure.

Before these experiments were commenced or the literature searched, the author held, as a working hypothesis, that the most symmetrical molecular structures should give rise to the most symmetrical crystallographic forms, although the converse would not necessarily be true. Thus, the most symmetrical of all types, namely, the type CX_4 , in which X is an element or symmetrical group such as CH_3 , and which itself possesses cubic symmetry (although not the highest symmetry possible in that system) should give rise to crystals of the cubic system; whilst compounds of this type in which X is a less symmetrical group should give rise to tetragonal crystals. Considered as an expression of what is undoubtedly a strong general tendency, this hypothesis* is fully borne

* This rule has already been of service in providing evidence of constitution. The synthesis of methanetetra-acetic acid has recently been described by Ingold and Nickolls (*T.*, 1922, **121**, 1645) and its crystallographic properties are given on p. 78. When this acid was first prepared there was doubt as to its constitution, which might have been that corresponding with any one of the formulae $C(CH_2CO_2H)_4$, $(CO_2HCH_2)_4CHCH(CO_2H)_2CH_2CO_2H$, and $CO_2HCH_2CH_2C(CO_2H)_2CH_2CO_2H$. The crystallographic evidence points to

out by the evidence brought forward in this paper and is in agreement with the conclusions drawn by Wahl (*Proc. Roy. Soc.*, 1914, [A], 90, 1) as a result of the optical investigations of a number of simple carbon compounds. The modifications necessary in its detailed application will be discussed hereunder.

The first case which has to be considered is that in which X is a single univalent element. There are four examples on record: Wahl has examined the crystalline form of methane (*ibid.*, 1912, [A], 87, 377) and of carbon tetrachloride (*ibid.*, 1913, [A], 89, 330), Wahl (*loc. cit.*) and Zirngiebl (Groth, "Chem. Kryst." I, 330) carbon tetrabromide, and Gustavson (*op. cit.*, p. 229; *Annalen*, 1874, 172, 173) carbon tetraiodide. Methane itself crystallises below -185.8° in the cubic system. Carbon tetrachloride at -22° crystallises in grains, which are isotropic and therefore belong to the cubic system, but at -47° a transition into a doubly refracting mass takes place.

Carbon tetrabromide crystallises in the cubic system above 46° , there being a transition at that temperature into a monoclinic variety, which, however, has a marked cubic habit, the crystals very closely approaching regular octahedra. Carbon tetraiodide crystallises in octahedra, which are isotropic and therefore cubic in symmetry; no accurate measurements have been made owing to the unstable character of the compound.

There does not appear to be an example of a substance CX_4 in which X is a group of two atoms, but an instance of one in which X is a group of three atoms is provided by tetranitromethane, which has been examined by Wahl (*Proc. Roy. Soc.*, 1913, [A], 89, 333). This substance crystallises in the cubic system, although at low temperatures there is a transition into a modification which shows very weak double refraction and probably belongs to a uniaxial system. Of compounds in which X is a group of four atoms, one of which must necessarily be carbon or some other quadrivalent element, an example is afforded by tetramethylmethane, which Wahl (*ibid.*, 1913, [A], 88, 359) found to be cubic, with a low-temperature, doubly refracting modification, which is probably tetragonal.

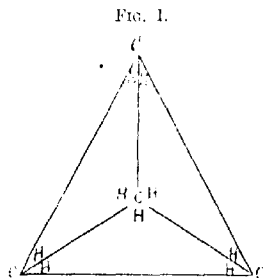
In all these cases, in agreement with the original hypothesis, the crystalline form stable at the higher temperature is cubic. The lower-temperature modification with a lower degree of symmetry shown by four of these compounds may reasonably be supposed to

plainly to a formula of the type CX_4 . The first formula was therefore accepted by the investigators concerned as a satisfactory basis for further work and was fully confirmed several months later by purely chemical methods (*loc. cit.*).

be due to a closer packing of the molecular units at lower temperatures.*

The symmetry of a molecule of the type CX_4 , in which X is a single atom, is that of a regular tetrahedron, that is, of Evans's CBU (hexakis tetrahedral) class of the cubic system, possessing therefore six diagonal planes of symmetry, the four trigonal symmetry axes of the cubic system, and three digonal axes of ordinary symmetry, which are also tetragonal "contra-directional" (Evans, *Min. Mag.*, 1910, 398) axes or Hilton's (*ibid.*, 1906, 261) axes of the second sort. It might be expected therefore that compounds of this type would crystallise with cubic symmetry, as has actually been found.

Since each of the bonds from the central carbon atom represents one of the four axes of trigonal symmetry essential to all classes of the cubic system, compounds of the type CX_4 , in which X is a group of such a nature as not to destroy the trigonal symmetry about these bonds, should yield cubic crystals. The compound tetramethylmethane, $C(CH_3)_4$, is one of these, three hydrogen atoms being arranged symmetrically about a carbon atom at each corner of the tetrahedron (Fig. 1). It is consistent therefore to find this compound crystallising in the cubic system.



In the compound tetranitromethane, $C(NO_2)_4$, the configuration of the nitro-group is uncertain beyond that the nitrogen atom is directly attached to the carbon atom. Of the possible configurations, the linear arrangement, $\cdot N \cdot O \cdot O$, is the only one which would allow of the persistence of the four trigonal axes and so lead to the expectation of cubic crystals, as actually found.

Turning now to more complex cases, pentaerythritol, $C(CH_2OH)_4$, has been examined by Martin (*Neues Jahrb. Min.*, 1891, Beil. Bd. 7, 18) and found to be tetragonal and to crystallise in the ditetragonal-pyramidal class, that is, the IV Bu class of Evans (*Min. Mag.*, 1907, 360) and therefore to possess a uniterminal axis. The author examined this compound at Cambridge in 1918, and, after repeated

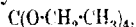
* An analogy with this behaviour is to be found in that of the minerals andalusite and kyanite, both of which have the chemical composition Al_2SiO_5 . Andalusite possesses orthorhombic symmetry, and kyanite only triclinic symmetry. The density of kyanite (3.62) is higher than that of andalusite (3.18), which would indicate closer packing in the less symmetrical variety.

experiments, was unable to find the existence of a uniterminal axis or to assign other than the symmetry of Evans's IV Bc (holohedral) class to the crystals.

Pentaerythritol tetrabromide was found by Jaeger (*Z. Kryst. Min.*, 1908, **45**, 543) to belong to Evans's II Cc class (holohedral) of the monoclinic system. He regards the symmetry as pseudo-cubic, since by a suitable transformation of face symbols an axial ratio of nearly 1 : 1 : 1 and an axial angle of nearly 90° may be obtained.

Pentaerythritol tetranitrate, pentaerythritol tetra-acetate, and methanetetra-acetic acid all crystallise with tetragonal symmetry and with the exception of pentaerythritol tetra-acetate, in which the class is uncertain, in Evans's IV Bc (holohedral) class. They are described in the experimental part of this paper.

Tetraethyl orthocarbonate,



according to Wahl crystallises in the tetragonal system and is pseudo-cubic.

Tetraphenylmethane has been examined by Wahl (*Proc. Roy. Soc.*, 1913, [A], **89**, 338), who describes the crystals as needles which optically appear to be orthorhombic.

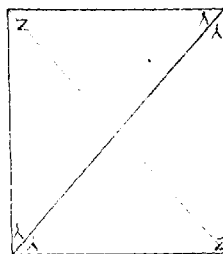
Of these seven compounds in which X is a complex group, five crystallise in the tetragonal system. Of the remaining two, tetraphenylmethane,

crystallising in the orthorhombic system, is perhaps a special case, in which the four phenyl groups have the predominant influence. Pentaerythritol tetrabromide, however, does appear to be an exception to the general rule, though it might be contended that it has a tendency towards a more symmetrical structure as shown by its pseudo-cubic nature.

In molecules of the type CX_4 , in which the X groups are of the type CY_2Z , it can easily be seen that the trigonal axes can no longer remain, for there can be no three-fold grouping about the corners of the tetrahedron. The symmetry is reduced to that of Evans's IV Bk (scalenehedral) class of the tetragonal system,* as shown in Fig. 2, which represents the appearance of such a molecule projected on the basal plane.

* E. von Federoff (*Z. Kryst. Min.*, 1913, **52**, 22) explained the lack of cubic symmetry in crystals of compounds such as pentaerythritol, as due to the carbon atom having a form which is only an approximation to a regular tetrahedron. In the same paper he put forward the view that the "crystal molecule" is composed of several chemical molecules.

FIG. 2.

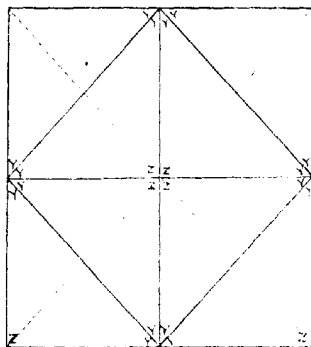


By the combination of four such molecular cells in the manner shown in Fig. 3, the symmetry is raised to that of Evans's IV Bu (ditetragonal-pyramidal) class of the tetragonal system, which possesses a uniterminal tetragonal axis and in which, therefore, crystals are unlike at the two ends of that axis.

By a further combination of two such complex cells, one inverted with respect to the other, holohedral tetragonal symmetry, that is, the symmetry of Evans's IV Bc class, may be reached. Such combinations of cells may be regarded as analogous to the ultra-microscopic twinning, considered to be the cause of the assumption of higher symmetry in certain minerals.

From these considerations it might reasonably be expected that compounds of the type $C(CY_2Z)_4$ * would crystallise in any of the

Fig. 3.



classes IV Bk, IV Bu, IV Bc of the tetragonal system. As already stated above, with the exception of pentaerythritol tetrabromide, the remaining five compounds of this type known all crystallise in the tetragonal system and in the case of three of them in the IV Bc (holohedral) class. In the case of two of them, namely, pentaerythritol tetraacetate and tetraethyl orthocarbonate, the class has not certainly been determined.

That tetraethyl orthocarbonate should be included with the compounds of the type $C(CY_2Z)_4$ needs perhaps a little explanation. From its structural formula, co-linear oxygen linkings being assumed, it is evident that the groups at the corners of the tetrahedron are of the type CY_2Z . The linking of each of these groups to the central carbon atom by way of an oxygen atom does not affect the symmetry of the molecule.

Pentaerythritol constitutes a particularly interesting example, since apparently it may assume either the symmetry of the IV Bu (ditetragonal-pyramidal) class as observed by Martin (*loc. cit.*) or that of the IV Bc (holohedral) class as observed by the author.

* It will be seen that in the compounds here discussed Y is hydrogen and, with one exception (in which it is bromine), Z is a complex group, but one which can be so symmetrically arranged as to be equivalent to a single atom as far as the symmetry of a molecule of this type is concerned. The latter will always be the case, provided that Z has a plane of symmetry.

As far as the compounds discussed in this paper are concerned, there is strong evidence that their crystallographic symmetry is an expression of their molecular structure, since from the consideration of their molecular configurations (where these are known) the observed crystallographic symmetry may be deduced. Should this be found by further research to be the case for a large number of organic compounds, it would become legitimate to employ crystallographic evidence in determining stereochemical configurations in cases where these have not yet been determined by chemical methods.

Other compounds of the type CX_4 are in course of preparation for this investigation, and it is proposed also to examine compounds of the type CXY_3 and CX_2Y_2 .

EXPERIMENTAL.

Pentaerythritol Tetranitrate, $C(CH_2O\cdot NO_2)_4$.

This compound was submitted to me for examination by Sir William Pope and measured by myself at Cambridge in 1918, when working under Dr. Hutchinson's direction.

Crystal system: tetragonal. Class: holohedral. Axial ratio: $a:c = 1:0.506$. Forms observed: $A = \{100\}$; $p = \{111\}$.

Angle measured:

	No. of measurements.	Limits.	Mean obs.	Calc.
$Ap = (100):(111)$	16	$65^\circ 37' - 65^\circ 46'$	$65^\circ 42'$	$65^\circ 42'$
$pp = (111):(111)$	11	$48^\circ 32' - 48^\circ 40'$	$48^\circ 36'$	*

Cleavage: $\{100\}$, imperfect.

Habit: square, second-order prism terminated by pyramids (Fig. 4). The crystals are colourless and transparent and of a fair size and quality.

Optical characters: refractive indices, as determined by immersion in oils, $\omega = 1.554$, $\epsilon = 1.553$.

Density: determined by suspension in liquid, $d_4^{20} = 1.773$ (corr.).

Pentaerythritol Tetra-acetate, $C(CH_2O\cdot CO\cdot CH_3)_4$.

Crystal system: tetragonal. Class: uncertain. Axial ratio: $a:c = 1:0.324$. Forms observed: $A = \{100\}$, $p = \{111\}$.

Cleavage: perfect basal.

Habit: long, narrow, second-order prisms terminated by blunt or sharp pyramids (Fig. 5). The crystals are colourless and transparent, but extremely small and badly developed. The pyramid faces, when distinguishable, are very minute and the only angular measurement obtainable has been from a face of the blunt

pyramid $p = \{111\}$ on to the prism $A = \{100\}$, this angle being $72^\circ 53'$.

Optical characters: refractive indices, as determined by immersion in oils, $\epsilon = 1.483$, $\omega = 1.433$.

Density: determined by suspension in liquid, $d_4^{20} = 1.213$ (corr.).

FIG. 4.

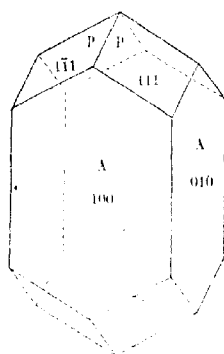
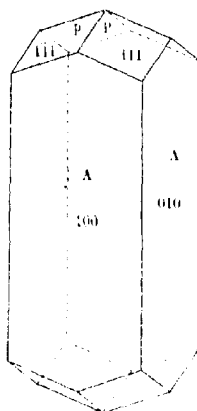


FIG. 5.



Methanotetra-acetic Acid, $C(CH_2CO_2H)_4$.

Crystal system: tetragonal. *Class*: holohedral. *Axial ratio*: $a : c = 1 : 0.560$. *Forms observed*: $m = \{110\}$, $p = \{111\}$.

Angle measured:

	No. of measurements.	Limits.		Mean obs.	Calc.
$pp = \{111\} : \{111\}$	9	$76^\circ 23\frac{1}{2}'$	$76^\circ 59\frac{1}{2}'$	$76^\circ 45'$	$76^\circ 47'$
$pp = \{1\bar{1}1\} : \{1\bar{1}1\}$	9	$102^\circ 59'$	$103^\circ 34\frac{1}{2}'$	$103^\circ 11'$	$103^\circ 13'$
$pm = \{111\} : \{110\}$	12	$51^\circ 20\frac{1}{2}'$	$51^\circ 49'$	$51^\circ 33\frac{1}{2}'$	$51^\circ 36\frac{1}{2}'$
$pp = \{111\} : \{1\bar{1}1\}$	19	$51^\circ 51'$	$52^\circ 18'$	$52^\circ 6'$	*
$pp = \{111\} : \{1\bar{1}\bar{1}\}$	13	$127^\circ 45\frac{1}{2}'$	$128^\circ 5'$	$127^\circ 54\frac{1}{2}'$	$127^\circ 54'$

Cleavage: none observed.

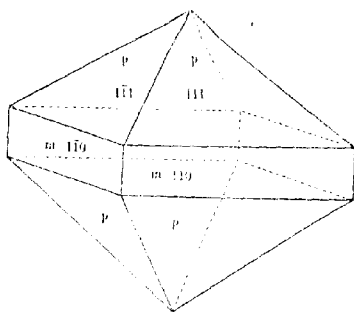
Habit: pyramidal, with short, first-order prisms (Fig. 6). The crystals are extremely small but moderately well developed and are clear and colourless.

Optical characters: refractive indices, as determined by immersion in oils, $\epsilon = 1.518$, $\omega = 1.487$.

Density: determined by suspension in liquid (carbon tetrachloride and light petroleum), $d_4^{20} = 1.460$ (corr.).

I desire to express my thanks to Dr. J. W. Evans for his kind help and interest in this work. I am also greatly indebted to the Organic Chemistry Department of the Imperial College, and especially to Dr. C. K. Ingold, for much helpful interest and for the facilities which they are offering in the preparation of compounds for this investigation. My thanks are, moreover, due to Colonel Lyons and the authorities of the Science Museum for their kindness in lending valuable apparatus, without which this work could not have been undertaken.

FIG. 6.



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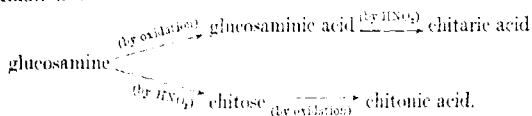
SOUTH KENSINGTON.

[Received, November 1st, 1922.]

N.—Elimination of the Amino-group of Tertiary Amino-alcohols. Part I.

By ALEX. MCKENZIE and ANGUS CAMPBELL RICHARDSON.

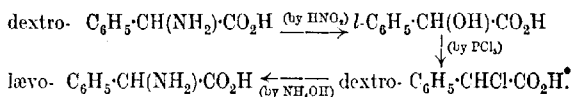
THE present investigation was initiated in connexion with an inquiry on the rôle of nitrous acid in the Walden inversion. Fischer was the first to give the definite proof that nitrous acid can induce configurative change when he effected the following transformations :



Thus, starting from the amino-sugar, it is possible to obtain the two epimeric 2:5-anhydrohexoic acids, and a Walden inversion had obviously been effected by one of the two reactions in which nitrous acid was concerned, probably, according to Levene (*Monographs of the Rockefeller Institute for Medical Research*, 1922, No. 18,

p. 15), during the elimination of the amino-group of glucosaminic acid.

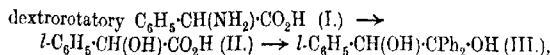
The displacement of the amino-group in dextrorotatory phenyl-aminoacetic acid leads to a change of sign owing to the formation of *l*-mandelic acid (McKenzie and Clough, T., 1909, 95, 791), and the following changes are involved in the interconversion of the optically active amino-acids:



At the time when this inversion was described the view was expressed with reserve that one of the three reagents, nitrous acid, phosphorus pentachloride, and ammonia, causes configurative alteration, the suggestion being made that the inversion is effected by means of the ammonia, both phosphorus pentachloride and nitrous acid thus acting "normally." The other alternative, that a configurative change takes place at each of the three stages, was regarded as improbable. In a subsequent paper, however, Clough (T., 1918, 113, 526) assumes that the levorotatory phenyl-aminoacetic acid and *l*-mandelic acid possess the same configuration, his arguments being based on the influence of inorganic salts on the rotatory powers of α -hydroxy- and α -amino-acids. Nevertheless, the configurative relationship between the active phenylaminoacetic and mandelic acids is almost as problematical as ever. Here as in other cases the same difficulty is still encountered to which both Fischer and one of us have made occasional references, and to which Frankland also drew attention in his presidential address to this Society in 1913 (T., 103, 738) when he writes, "It would appear that there does not exist at the present time any criterion whereby the relation between the configuration of an optical active compound and that of a derivative from it can be decisively ascertained."

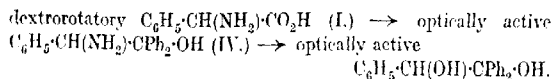
Now *l*-mandelic acid can be converted into the alcohol (to which the nomenclature *l*-triphenylethylene glycol was assigned) by forming the methyl *l*-ester which was then acted on by magnesium phenyl bromide (McKenzie and Wren, T., 1910, 97, 473). Although this glycol possesses a strong dextrorotation, the value being so high as $[\alpha]_D + 233.6^\circ$ in chloroform, there is no possibility of configurative change in its formation, since substitution of a group in direct attachment to an asymmetric carbon atom does not occur. Moreover, it can be formed in another way through the stages, *l*-mandelic acid \rightarrow methyl *l*-mandelate \rightarrow *l*-benzoin \rightarrow

l-triphenylethylene glycol (*loc. cit.*), whilst the isomeric *d*-triphenylethylene glycol was obtained as one of the products from the interaction of magnesium phenyl bromide and *l*-phenylchloroacetic acid (McKenzie, Drew, and Martin, T., 1915, 107, 26). Accordingly in the steps:

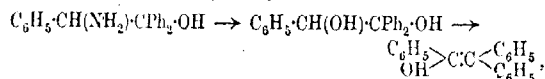


the conversion of I into II may possibly be accompanied by configurative alteration, whilst the configuration of II and III is identical.

It had been the intention of the present authors to convert I into IV, and then to examine the action of nitrous acid on this β -hydroxy- $\alpha\beta$ -triphenylethylamine to find out which of the isomeric optically active glycols would be the product:



With this object in view, and in order to gain experience with the inactive amino-alcohol before applying the results to the active isomerides, the inactive amino-alcohol was prepared by acting on ethyl *dl*-phenylaminoacetate or its hydrochloride with magnesium phenyl bromide. Its behaviour towards nitrous acid was then studied. On no occasion were we able to obtain triphenylethylene glycol by this means, but the product was invariably the so-called triphenylvinyl alcohol.* This interesting result would on first consideration find a ready interpretation on the lines:

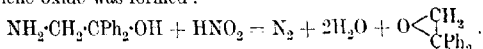


but this is untenable, because the experimental conditions are known under which triphenylvinyl alcohol can be obtained by the dehydration of triphenylethylene glycol (McKenzie and Wren, *loc. cit.*), and in the case under investigation the glycol would not have undergone dehydration had it been formed. Whatever the mechanism of the formation of triphenylvinyl alcohol by this action may be, the assumption of the intermediate production of triphenylethylene glycol is not permissible. The optically active β -hydroxy- $\alpha\beta$ -triphenylethylamine would certainly also give tri-

* The terminology triphenylvinyl alcohol is retained in the present paper, although the ketonic structure is probably more correct. The constitution of triphenylvinyl alcohol was recently discussed by McKenzie and Boyle (T., 1921, 119, 113).

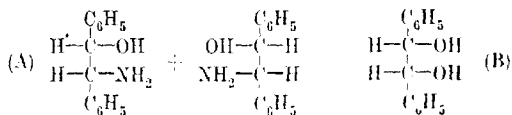
phenylvinyl alcohol when acted on by nitrous acid, and its preparation was accordingly abandoned for the present.

The above mode of formation of triphenylvinyl alcohol recalls the behaviour of nitrous acid towards diphenylaminomethylcarbinol (Paal and Weidenkaff, *Ber.*, 1906, **39**, 2062), when *as*-diphenylethylene oxide was formed:



The stable *as*-diphenylethylene glycol, which readily results from the interaction of ethyl glycolate and magnesium phenyl bromide, was not produced from the amino-alcohol.

As having a bearing on those observations, mention may be made of the experience of Erlenmeyer, jun., in the course of his work on the hydroxydiphenylethylamines (*Annalen*, 1899, **307**, 113). Inactive β -hydroxy- α , β -diphenylethylamine (A),

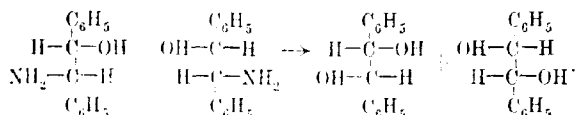


would be expected with nitrous acid to give the internally compensated hydrobenzoin (B) in the event of no configurative change occurring, but Erlenmeyer succeeded in isolating the externally compensated isomeride, the so-called *iso*-form. This reaction, differing as it does from the behaviour of β -hydroxy- α , β -triphenylethylamine towards nitrous acid, resembles it in being unexpected, and it should further be noticed in the same connexion that Irvine and Fyfe (*T.*, 1914, **105**, 1642) give experimental evidence in favour of their statement that the hydroxy-amine has a distinct tendency to react in the cyclic form, $\begin{array}{c} \text{CHPh}(\text{O}) \\ | \\ \text{CHPh}\cdot\text{NH}_2 \end{array}$.

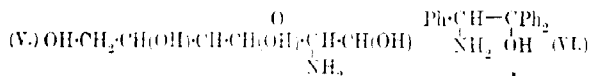
Now in an investigation with the isomeric dibromosuccinic acids (*T.*, 1912, **101**, 1196), one of us pointed out that configurative change with optically inactive materials by a process closely analogous to a Walden inversion* can take place (for other cases, compare Walden, "Optische Umkehrerscheinungen," Braunschweig, 1919, p. 98). The above result of Erlenmeyer is a change of this kind, and the proximity of the hydroxy- and amino-groups in the molecule is a factor of importance. If Erlenmeyer's suggestion is accepted that a transient compound, $\begin{array}{c} \text{C}_6\text{H}_5\text{C}(\text{H})(\text{OH}) \\ | \\ \text{C}_6\text{H}_5\text{C} \begin{array}{c} \diagup \\ \text{N} \\ \diagdown \end{array} \end{array}$

* The term "Walden inversion" should be strictly confined to changes effected with optically active compounds only (see footnote, *loc. cit.*, p. 1198).

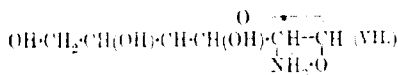
is formed, then the following interpretation is feasible. When nitrogen is eliminated from this hypothetical compound which contains only one asymmetric carbon atom and when water is then added, the product will contain two asymmetric atoms, and would be expected to consist of a mixture of hydrobenzoin and isohydrobenzoin in unequal amounts. Evidence in favour of this view is actually presented by Erlenmeyer himself, who on one occasion isolated together with isohydrobenzoin a few crystals of hydrobenzoin which were identified by crystallographic measurements (*loc. cit.*, p. 130). On the other hand, in the molecule of the *iso*-base the spatial arrangement of the hydroxy- and amino-groups is presumably such that they are further apart than in the isomeride, and the action of nitrous acid is more likely to be one of direct displacement. As a matter of fact Erlenmeyer showed that the action of nitrous acid proceeds in the orthodox fashion with the *iso*-base, the product being isohydrobenzoin, which, like the *iso*-base, is externally compensated:



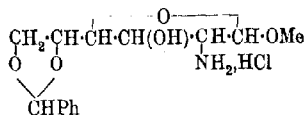
Attention may also be directed to the behaviour of *d*-glucosamine towards nitrous acid because the parallel between this action and the formation of triphenylvinyl alcohol from β -hydroxy- $\alpha\beta$ -triphenylethylamine is closer than would at first sight be suggested by a perusal of the formulae:



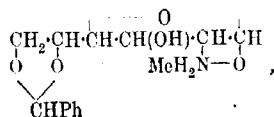
(VI) differing from (V) in being a tertiary alcohol. Glucosamine loses its nitrogen atom, passing into the anhydro-hexose, $\text{C}_6\text{H}_{10}\text{O}_5$, to which the name chitose was assigned by Ledderhose, and which according to Levene (*loc. cit.*, p. 16) is 2:5-anhydromannose. A hexose itself is not produced, just as triphenylethylene glycol is not formed in the action studied by us. It should also be noted that Irvine and Hynd (T., 1912, 101, 1128, and other papers), in the course of their investigations on derivatives of glucosamine, propose a betaine-like structure for this base, namely,



Moreover, the same authors examined the effect of silver nitrite on an aqueous solution of benzylidenemethylglucosamine hydrochloride, .



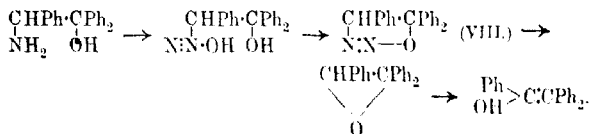
where the amino-group, the benzyldene residue, and the glucosidic group were all eliminated, a process in which the tautomeric form,



would probably be produced before the action of nitrous acid came into play.

The adoption of a betaine-like structure for β -hydroxy- $\alpha\beta$ -triphenylethylamine should not, therefore, be at once dismissed, the formulation, $\text{CHPh} \cdot \text{CPh}_2$, being more closely related to the betaine-like structure of glucosamine (VII) than is (VI) to (V). Our experimental evidence would, however, be rather in favour of retaining formula (VI).

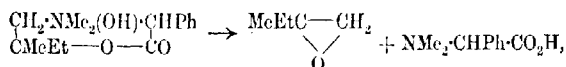
The most likely interpretation of the formation of triphenylvinyl alcohol from the amino-alcohol seems to us to be the following, which involves the intermediate formation of an unstable furo-diazole derivative (VIII):



As an alternative to (VIII), although perhaps less feasible, the assumption of an unstable substance of a betaine-like structure might be made, thus, $\text{N}:\text{N} < \text{CHPh} > \text{CPh}_2$. A structure like this would be related to that for diazo-phenols advocated by Klemenec (*Ber.*, 1914, **47**, 1407) when he rejects both the diazo-oxide and the quinonediazide structures for those compounds in favour of the diazonium type. It should be observed, however, that Klemenec's conclusion has not been accepted by other workers in the same

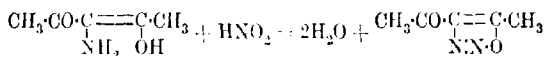
field (Morgan and Porter, T., 1915, **107**, 645; Morgan and Evens, T., 1919, **115**, 1126).

The scission of the ring (VIII) with elimination of nitrogen seems possible, and may be contrasted with the observation of Fourneau (*Bull. Soc. chim.*, 1908, [iv], **3**, 1141) on the action of alkali on phenylmethylethylmorpholonedimethylammonium hydroxide,



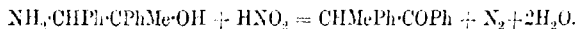
where *as*-methylethylethylene oxide, as distinct from triphenylethylene oxide, is sufficiently stable as to permit of its isolation.

Some support is perhaps lent to the scheme suggested above from the fact that diazo-oxides have been isolated by the action of nitrous acid on amino-1 : 3-diketones, for example, in the formation of acetylacetone diazoanhydride, where aminoacetylacetone reacts in accordance with its enolic structure :



(Wolff, *Annalen*, 1902, **325**, 139).

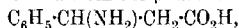
In the present paper, the elimination of the amino-group of several other tertiary amino-alcohols is also described. Thus, β -hydroxy- $\alpha\beta$ -diphenylpropylamine, prepared from desylamine hydrochloride and magnesium methyl iodide according to McKenzie and Barrow (T., 1913, **103**, 1331), gave methyldeoxybenzoin, and not $\alpha\beta$ -dihydroxy- $\alpha\beta$ -diphenylpropane :



Similarly from β -hydroxy- $\alpha\beta$ -diphenyl- β -naphthylethylamine, $\text{NH}_2\cdot\text{CHPh}\cdot\text{CPh}(\text{C}_{10}\text{H}_7)\cdot\text{OH}$, the compound obtained by the action of nitrous acid was either naphthyldeoxybenzoin or one of its desmotropic isomerides.

γ -Hydroxy- $\alpha\gamma$ -triphenylpropylamine, $\text{NH}_2\cdot\text{CHPh}\cdot\text{CH}_2\cdot\text{CPh}_2\cdot\text{OH}$, prepared by the action of magnesium phenyl bromide on ethyl β -amino- β -phenylpropionate, has a methylene group interposed between the carbon atoms to which the amino- and hydroxy-groups are respectively attached, and in this case the action of nitrous acid presents no abnormality, as the product was found to be $\alpha\gamma$ -dihydroxy- $\alpha\gamma$ -triphenylpropane, $\text{OH}\cdot\text{CHPh}\cdot\text{CH}_2\cdot\text{CPh}_2\cdot\text{OH}$. On the other hand, with γ -hydroxy- $\alpha\gamma$ -triphenylisopropylamine, $\text{CH}_3\text{Ph}\cdot\text{CH}(\text{NH}_2)\cdot\text{CPh}_2\cdot\text{OH}$, prepared from magnesium phenyl bromide and the hydrochloride of phenylalanine ethyl ester, the spatial arrangement of the amino- and hydroxy-groups is similar.

to that in *p*-hydroxy- $\alpha\beta\beta$ -triphenylethylamine, and the action of nitrous acid accordingly led to a compound which in all probability is diphenylmethyl benzyl ketone, $\text{CH}_2\text{Ph}\cdot\text{CO}\cdot\text{CHPh}_2$, the desmotropic form of diphenylbenzylvinyl alcohol. The isomeric amino-alcohols, the one derived from the β -amino-acid,



and the other from the α -amino-acid, $\text{C}_6\text{H}_5\cdot\text{CH}_2\cdot\text{CH}(\text{NH}_2)\cdot\text{CO}_2\text{H}$, thus presented an interesting contrast in their behaviour on elimination of the amino-group.

EXPERIMENTAL

Conversion of Phenylaminoacetic Acid into β -Hydroxy- $\alpha\beta\beta$ -triphenylethylamine.

The phenylaminoacetic acid was prepared by a modification of the method of Zelinsky and Stadnikoff (*Ber.*, 1906, **39**, 1722; 1908, **41**, 2063). The free amino-acid (1 mol.) was acted upon by an excess of magnesium phenyl bromide (4 mols.), but on decomposing the product in the usual manner with ammonium chloride, the acid was found to be regenerated. The hydrochloride of the ethyl ester was accordingly prepared, and this melted at 196–197° in accordance with Kossel's value (*Ber.*, 1891, **24**, 4145). 16.6 Grams of ethyl phenylaminoacetate hydrochloride (1 mol.) were added in five instalments within fifteen minutes to the Grignard reagent prepared from 145 grams of bromobenzene (12 mols.), and the mixture was heated for four and a half hours. Ice was added, and then ammonium chloride. The solid remaining undissolved after this treatment was left in contact over-night with ammonium chloride and ammonia, and then collected. The resulting 24 grams were crystallised from ethyl alcohol. Yield of pure compound = 9 grams. The ethereal solution, from which the ether and diphenyl were removed, gave an additional quantity of the amino-alcohol. Total yield = 11 grams, 49 per cent. of the theoretical (Found: C = 82.7; H = 6.6. Calc., C = 83.0; H = 6.6 per cent.).

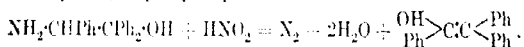
The substance melted at 154.5–155°, and was identical with the β -hydroxy- $\alpha\beta\beta$ -triphenylethylamine prepared by McKenzie and Barrow (*loc. cit.*) from desylamine hydrochloride and magnesium phenyl bromide. It is sparingly soluble in ethyl alcohol, from which it separates in needles. It is sparingly soluble in ether, and moderately soluble in benzene or carbon disulphide. With concentrated sulphuric acid, it gives a pink coloration which quickly becomes orange-brown. Its hydrochloride, which is sparingly soluble in water, melts at 236–237°.

In order to obtain the amino-alcohol in good yield by the above method, the Grignard reagent must be employed in the large excess quoted. In three other earlier experiments in which the bromobenzene in the proportion of 5 mols. to 1 mol. of the ester hydrochloride was employed, the average yield of the pure amino-alcohol was only slightly over one-fifth of the weight of hydrochloride taken. A good yield of amino-alcohol was also obtained from ethyl phenylaminoacetate by using a large excess of magnesium phenyl bromide to which an ethereal solution of the ester was added. The ester was prepared from the free amino-acid, and boiled at 135°/15 mm., whereas Marvel and Noyes (*J. Amer. Chem. Soc.*, 1920, **42**, 2265) give 114–115°/5 mm. From 135 grams of bromobenzene (12 mols.) and 13.4 grams of ester (1 mol.), 9 grams of the pure amino-alcohol were isolated. This is also an instructive instance of the application of a Grignard reagent in this respect, that the results were successful only when an exceptionally large proportion of the reagent was employed.

Unfortunately we failed to isolate a crystalline product either when the Grignard reagent prepared from 66 grams of methyl iodide (12 mols.) was added to 10.5 grams of the ester hydrochloride (1 mol.) suspended in ether, or when the addition was conducted in the reverse order. With magnesium α -naphthyl bromide, prepared from 75 grams of α -bromonaphthalene (12 mols.), and 6.24 grams of ester hydrochloride (1 mol.), 1.2 grams of a substance, melting at 65.5–66.5°, and crystallising from ethyl alcohol in colourless, lustrous plates, were isolated (Found: C = 83.1; H = 6.3 per cent.). This compound contained no nitrogen, and was, accordingly, not the desired amino-alcohol. In those cases the actions obviously proceeded too tardily, and were incomplete, in spite of the large excess of Grignard reagents used.

Action of Nitrous Acid on β -Hydroxy- $\alpha\beta$ -triphenylethylamine.

Several attempts were made to obtain triphenylethylene glycol by the action of nitrous acid on the above compound, but in no case was there any evidence that the glycol was formed, the product invariably being triphenylvinyl alcohol:



Thus, 5 grams of β -hydroxy- $\alpha\beta$ -triphenylethylamine (1 mol.) were dissolved by heating with 300 c.c. of dilute acetic acid, and to the ice-cold solution 19 c.c. of an aqueous solution of sodium nitrite containing 3.6 grams of the salt (3 mols.) were added in the course of half an hour. On the following day the voluminous precipitate

(3.5 grams, m. p. 128—136°) was collected, and crystallised from ethyl alcohol. 3.2 Grams of triphenylvinyl alcohol, m. p. 135—136°, crystallising in needles and giving the diagnostic emerald-green coloration with concentrated sulphuric acid, were isolated: yield = 68 per cent. (Found: C = 88.1; H = 6.0. Calc., C = 88.2; H = 5.9 per cent.).

Action of Nitrous Acid on β -Hydroxy- $\alpha\beta$ -diphenylpropylamine.

The amino-alcohol was prepared by acting on desylamine hydrochloride with magnesium methyl iodide (McKenzie and Barrow, *loc. cit.*). It gives a pink coloration with concentrated sulphuric acid, and forms a hydrochloride which is sparingly soluble in water and which melts at 262°.

An aqueous solution of sodium nitrite (3 mols.), 17 c.c. containing 3.7 grams of salt, was gradually added within forty-five minutes to an ice-cold solution of 4 grams of β -hydroxy- $\alpha\beta$ -diphenylpropylamine (1 mol.) in 230 c.c. of dilute acetic acid. After neutralisation with sodium hydroxide, the liquid was extracted with ether, and the ethereal solution dried with anhydrous magnesium sulphate. The product from the ether was partly oily and partly solid. It was crystallised twice from ethyl alcohol, when 0.8 gram of methyldeoxybenzoin, separating in prisms, and melting at 59.5—60°, was obtained. A trace of this product gave practically no coloration with concentrated sulphuric acid at the ordinary temperature, but a pale green tint appeared on warming. The melting point of methyldeoxybenzoin given by V. Meyer and Oelkers is 53° (*Ber.*, 1888, **21**, 1297).

In another experiment where 3.4 grams of the amino-alcohol were employed, the product was crystallised six times from light petroleum (b. p. 60—70°), and then melted at 59—59.5°. Yield = 0.42 gram (Found: C = 85.8; H = 7.0. Calc., C = 85.7; H = 6.7 per cent.). The *semicarbazone* crystallises from ethyl alcohol or from benzene in prismatic needles, and melts at 161°.

The small yield of methyldeoxybenzoin quoted above, coupled with the fact that the crude product contained an oil, suggests that methyldeoxybenzoin may not have been the sole product of the reaction. It is not improbable that the isomeric diphenylmethylacetaldehyde, which was prepared by Tiffeneau and Dorlen-court by the dehydration of $\alpha\beta$ -dihydroxy- $\alpha\beta$ -diphenylpropane (*Ann. chim. phys.*, 1909, [viii], **16**, 237) and which is described by those authors as an oil, may also have been formed by the elimination of the amino-group of β -hydroxy- $\alpha\beta$ -diphenylpropylamine.

Action of Nitrous Acid on β -Hydroxy- $\alpha\beta$ -diphenyl- β -1 naphthylethylamine.

The amino-alcohol was prepared by acting on desylamine hydrochloride with magnesium α -naphthyl bromide (*loc. cit.*). To a cooled solution of the amino-alcohol (3.4 grams) in 50 per cent. acetic acid a solution of sodium nitrite (2 grams) in 11 c.c. of water was gradually added during twenty minutes. A white solid was precipitated during the addition, and some oil had also separated over-night. The mixture was made alkaline with sodium hydroxide and extracted with ether. The product from the ethereal solution was an oil, which was dissolved in hot light petroleum (b. p. 40—60°). Crystallisation started on cooling, and after one further crystallisation the product was pure. Yield = 2 grams. The compound, $C_{24}H_{18}O$, which is either naphthyldeoxybenzoin or one of its isomerides, is sparingly soluble in light petroleum (b. p. 40—60°), from which it separates in rectangular prisms, and melts at 107—108° (Found: C = 89.1; H = 6.0. Calc., C = 89.4; H = 5.6 per cent.).

The statement made by McKenzie and Barrow (*loc. cit.*), that β -hydroxy- $\alpha\beta$ -diphenyl- β -naphthylethylamine is converted by nitrous acid into the diphenyl- α -naphthyl glycol prepared by Acree from benzoin and magnesium α -naphthyl bromide (*Ber.*, 1904, **37**, 2764), is incorrect. The action of nitrous acid was conducted on that occasion in the presence of dilute hydrochloric acid, and the solid which separated was the crude hydrochloride melting with decomposition at a point close to that given by Acree for the glycol.

Action of Nitrous Acid on γ -Hydroxy- $\alpha\gamma\gamma$ -triphenylpropylamine.

Ethyl β -amino- β -phenylpropionate, prepared by esterifying β -amino- β -phenylpropionic acid (Posner, *Ber.*, 1905, **38**, 2316) with ethyl alcohol and hydrogen chloride, boiled at 149°/12 mm., whereas Fischer (*Ber.*, 1910, **43**, 2020) gives 150°/13 mm.

The preparation of the amino-alcohol presented difficulties, and the following conditions were ultimately arrived at. An ethereal solution of the ester (15 grams, 1 mol.) was gradually added to the Grignard reagent prepared from bromobenzene (98 grams, 8 mols.). After heating for nine hours, the additive compound was decomposed by ice and ammonium chloride, the ethereal solution dried by anhydrous magnesium sulphate, the ether expelled, and the residual oil triturated with light petroleum to remove the diphenyl, and then dissolved in hot ethyl alcohol. Over-night at about 5°, 2.7 grams of the crude amino-alcohol had separated, and after

two crystallisations from a mixture of benzene and light petroleum (b. p. 60—76°) 1.2 grams of the pure substance were obtained.

γ-Hydroxy-αγγ-triphenylpropylamine, $\text{NH}_2\text{-CHPh-CH}_2\text{-CPh}_2\text{-OH}$, separates from a mixture of benzene and light petroleum in prismatic needles, and melts at 146.5—147.5°. It may also be crystallised from ethyl alcohol, methyl alcohol, or ethyl acetate. It gives a reddish-orange coloration with concentrated sulphuric acid (Found: C = 82.8; H = 7.1. Calc., C = 83.1; H = 7.0 per cent.).

The solution of the amino-alcohol (0.67 gram, 1 mol.) in 40 c.c. of 50 per cent. acetic acid was cooled in a freezing mixture, and 3 c.c. of an aqueous solution of sodium nitrite (0.6 gram, 3 mols.) were gradually added within fifteen minutes. A flocculent precipitate (0.6 gram) separated. Over-night, this was crystallised from benzene, and then from a mixture of benzene and light petroleum. Yield = 0.3 gram; m. p. 127.5—128.5°. A trace of the substance when added to concentrated sulphuric acid became bright scarlet, and the solution had a pale orange tint. This colour reaction is distinctly different from that exhibited by *γ*-hydroxy-*xyγ*-triphenylpropylamine, and is identical with that of *αγ*-dihydroxy-*xyγ*-triphenylpropane, which had been prepared some years previously by McKenzie and Martin (T., 1913, 103, 114) by the interaction of magnesium phenyl bromide and *β*-hydroxy-*β*-phenylpropionic acid. The melting point of the compound, obtained as just described, was not depressed by admixture with some of the product prepared by McKenzie and Martin.

Action of Nitrous Acid on γ-Hydroxy-αγγ-triphenylisopropylamine.

Dry hydrogen chloride was passed through a mixture of phenylalanine (5.6 grams) and 100 c.c. of ethyl alcohol for one hour, and the mixture boiled for one hour longer. The solution was concentrated, and the resulting solid crystallised from a mixture of toluene and light petroleum. *Ethyl phenylalanine hydrochloride* crystallises in needles, and melts at 124—125°.

This ester hydrochloride (3.4 grams, 1 mol.) was gradually added within half an hour to the Grignard reagent prepared from bromobenzene (10.5 grams, 6 mols.). The mixture was heated for nine and a half hours, and the additive compound decomposed by ice and ammonium chloride. The undissolved solid was crystallised from ethyl alcohol, when 0.3 gram of the pure amino-alcohol was obtained. The ethereal solution from which the solid had been removed was heated to expel the ether, and the diphenyl was then removed by distillation in steam. The residual oil gradually solidified, and was then crystallised from ethyl alcohol. Total yield = 1.8 grams.

γ -Hydroxy- $\alpha\gamma\gamma$ -triphenylisopropylamine, $\text{CH}_2\text{Ph}\cdot\text{CH}(\text{NH}_2)\cdot\text{CPh}_2\cdot\text{OH}$, separates from ethyl alcohol in glassy needles, and melts at $144.5-145.5^\circ$ (Found: C = 83.0; H = 7.0. Calc., C = 83.1; H = 7.0 per cent.).

A solution of the amino-alcohol (1 gram) in 25 per cent. acetic acid was cooled in a freezing mixture, and an aqueous solution (5 c.c.) of 0.7 gram of sodium nitrite was added during forty-five minutes. A bulky, gelatinous solid (0.71 gram) was deposited, and this was crystallised twice from light petroleum (b. p. $40-60^\circ$). The product contained no nitrogen, and amounted to 0.33 gram.

The compound, $\text{C}_{21}\text{H}_{18}\text{O}$, which is probably diphenylmethyl benzyl ketone, separates from light petroleum in rosettes of glassy needles, and melts at $121.5-122^\circ$. It is readily soluble in ethyl alcohol and in benzene (Found: C = 88.2; H = 6.5. Calc., C = 88.1; H = 6.3 per cent.).

The thanks of the authors are due to the Carnegie Trust for the assistance rendered in the prosecution of this research.

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[Received, November 24th, 1922.]

XI.—*The Transition from the Colloidal to the Crystalloidal State. Solutions of Potassium Oleate.*

By LOUIS LEIGHTON BIRCUMSHAW.

It is a well-known fact that certain substances, for example, potassium oleate and tannic acid, form colloidal solutions in water; but in organic solvents such as alcohol or acetone, they give non-associated and practically non-dissociated solutions. This has been shown to be the case for potassium oleate (Laing, T., 1918, **113**, 435). The transition from colloid to crystalloid has been discussed in a theoretical paper by Witzemann (*J. Physical Chem.*, 1922, **26**, 3, 261), and it has always been assumed that the transition from the one to the other takes place gradually; but up to the present the question does not appear to have been investigated experimentally. In view of the extensive and important researches of McBain and his collaborators on the salts of the higher fatty acids, it was decided to commence the study of this transition with an investigation of the behaviour of potassium oleate in mixtures of water and alcohol, and the present communication deals with these solutions.

The experimental methods included determinations of the density, viscosity, and surface tension of a complete series of mixtures from

pure alcohol to pure water, each containing the same definite amount of the oleate.

EXPERIMENTAL.

Preparation of Materials.—Potassium oleate was prepared by neutralising pure oleic acid (Kahlbaum) with potassium ethoxide, prepared by dissolving potassium in absolute alcohol after washing it with ether. A few grams of this solution were diluted with alcohol and titrated with a dilute solution of known concentration of the oleic acid in alcohol, using phenolphthalein as an indicator. The main part of the potassium ethoxide solution was then carefully weighed and the calculated quantity of oleic acid added. A large quantity of the salt immediately separated out. The flask was cooled in ice-water, and the salt rapidly filtered off by the aid of the pump, washed twice with a small quantity of alcohol and once with ether, and dried in a vacuum desiccator. In this way it was obtained as a white, voluminous powder.

The alcohol was prepared by boiling rectified spirit with recently ignited lime for two days, distilling off, and boiling the distillate under reflux with calcium.

Densities.—The mixed solvents were made up by weight, and the solutions by volume in calibrated flasks at 25°. The densities were determined at 25° in a 20 c.c. pycnometer, corrected for buoyancy, and referred to water at 4°. The results are given in Table I.

TABLE I.

Densities.

P = Percentage of alcohol (by weight) in the solvent.

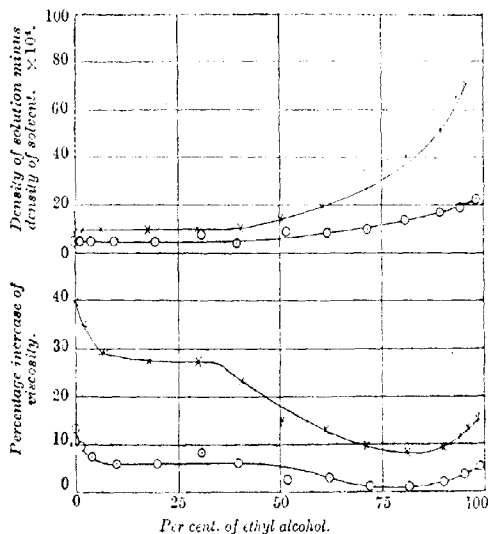
D₀ = Density of the mixed solvent. D₁ = Density of the solution.

1.0 Gram of potassium oleate in 100 c.c. of solvent.			3.2 Grams of potassium oleate in 100 c.c. of solvent.		
P.	D ₀ .	D ₁ .	P.	D ₀ .	D ₁ .
0.0	0.99707	0.99757	0.00	0.99707	0.99792
1.19	0.99485	0.99534	1.34	0.99457	0.99562
3.20	0.99122	0.99180	5.46	0.98743	0.98851
7.88	0.98365	0.98417	14.64	0.97384	0.97488
16.79	0.97091	0.97180	24.30	0.96002	0.96106
25.58	0.95804	0.95861	33.60	0.94416	0.94521
34.74	0.94196	0.94236	43.00	0.92516	0.92674
44.72	0.92146	0.92247	53.02	0.90303	0.90507
54.16	0.90042	0.90126	63.62	0.87853	0.88213
64.31	0.87690	0.87801	74.46	0.85265	0.85683
75.07	0.85117	0.85270	85.84	0.82446	0.82972
85.96	0.82415	0.82597	91.07	0.81074	0.81743
91.97	0.80831	0.81034	94.13	0.80236	0.80953
98.10	0.79099	0.79338			

In Fig. 1 the increase of density is plotted against the percentage (volume) of water in the mixed solvent.

Viscosities.—The viscosities were determined in a viscometer of the Oswald type, with a capacity of 18 c.c., and a capillary 6.8 cm. long and 0.053 cm. in diameter. The time of flow for water at 25° was 283 seconds. Great care was taken to keep the capillary free from dust and from the very fine particles of fibre which are usually found in solutions. Before making a measurement, each solution was allowed to settle for at least a week, and was then blown over into the instrument by means of dry dust-free air, purified from traces of carbon dioxide. The viscometer containing the solution

FIGS. 1 and 2.



was allowed to remain in the thermostat for twenty to thirty minutes before taking a measurement. The times were taken with a stop-watch reading to 0.2 of a second, and the thermostat was maintained at $25^\circ \pm 0.01^\circ$.

Several observers have detected changes in the viscosity of colloidal solutions with time. A $N/10$ -solution of the potassium oleate used in these experiments was found, however, to have a time of flow of 392 seconds at the beginning of August when freshly-prepared and of 391 seconds on October 16th, showing that this change does not occur in the solutions under investigation.

The results are given in Table II.

TABLE II.

Viscosities.

t = Time of flow of the solution (seconds).

 η_0 = Viscosity of the solvent. η_1 = Viscosity of the solution.

1.0 Gram of potassium oleate in 100 c.c. of solvent.				3.2 Grams of potassium oleate in 100 c.c. of solvent.			
P.	t.	η_0 .	η_1 .	P.	t.	η_0 .	η_1 .
0.0	319	890	1005	0.0	392	890	1240
1.19	334	955	1050	1.34	411	955	1290
3.20	362	1055	1135	5.46	481	1160	1500
7.88	432	1270	1345	14.64	652	1575	2010
16.79	583	1680	1785	24.30	817	1955	2480
25.58	714	1985	2165	33.60	913	2215	2720
34.74	798	2245	2375	43.00	924	2360	2705
44.72	827	2350	2410	53.02	996	2285	2590
54.16	822	2270	2340	63.62	841	2140	2340
64.31	774	2120	2145	74.46	760	1900	2055
75.07	704	1885	1895	85.84	654	1575	1710
85.96	610	1560	1590	91.07	606	1400	1565
91.97	554	1370	1420	94.13	574	1300	1470
98.10	481	1150	1205	97.39	536	1180	1355

In Fig. 2, the percentage increase of viscosity is plotted against the percentage (volume) of water in the mixed solvent.

Surface Tensions.—The surface tensions were determined in the modified Harkins apparatus which has already been described (T., 1922, 121, 887). The drops were blown out rapidly (two to three seconds) and allowed to hang from the tip for sixty seconds and then to fall under the influence of gravity. In this way, considerable time was allowed for the attainment of equilibrium at the surface. In each determination, thirty drops were collected and weighed and two determinations agreeing within 0.2 per cent. were made at every concentration. The results are shown in Table III.

In Fig. 3, the lowering of the surface tension is plotted against the percentage (volume) of water in the mixed solvent.

An interesting observation was that the lowering produced by a 1 per cent. solution of the oleate in water was greater than that produced by a 3.2 per cent. solution.

Discussion.

In order to explain the observed high conductivity and comparatively small osmotic effect exhibited by the salts of the higher fatty acids, McBain has put forward the theory that these solutions contain an ionic micelle or agglomeration of anions. To this complex ion, which is supposed to be heavily hydrated and to contain undissociated colloid, he assigns a high electrical but low mechanical mobility. In very dilute solutions, these salts are present as simple

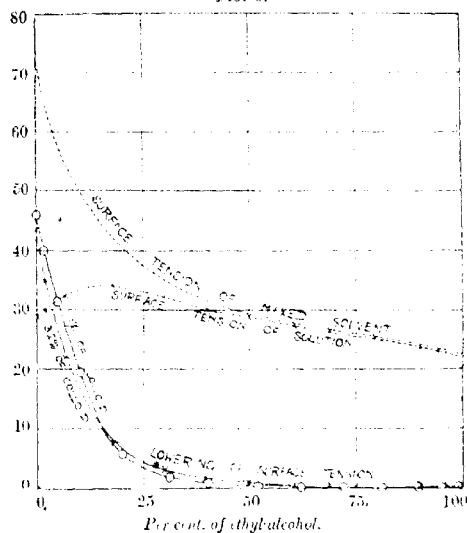
TABLE III.
Surface Tensions.

W — Weight of the drop.

σ_0 — Surface tension of the solvent. σ_1 — Surface tension of the solution.

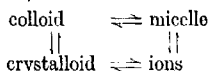
1.0 Gram of potassium oleate in 100 c.c. of solvent.				3.2 Grams of potassium oleate in 100 c.c. of solvent.			
P.	W.	σ_0 .	σ_1 .	P.	W.	σ_0 .	σ_1 .
0.00	0.03242	72.2	25.7	0.00	0.03573	72.2	28.6
1.19	0.03357	66.8	26.8	1.34	0.03715	65.0	29.8
3.20	0.03347	58.5	26.7	5.46	0.04000	54.0	32.2
7.88	0.03935	50.5	31.7	14.04	0.04192	42.0	33.8
16.79	0.04302	40.4	34.8	24.30	0.03992	35.2	32.2
25.58	0.04033	34.4	32.6	33.60	0.03725	31.6	30.0
34.74	0.03755	31.2	30.2	43.00	0.03540	29.2	28.5
44.72	0.03555	28.9	28.6	53.02	0.03391	27.6	27.0
54.15	0.03414	27.5	27.4	63.62	0.03279	26.4	26.1
64.31	0.03280	26.3	26.3	74.46	0.03144	25.0	24.9
75.07	0.03153	25.0	25.3	85.84	0.02993	23.7	23.6
85.96	0.03000	23.6	24.0	91.97	0.02915	23.3	23.0
91.97	0.02918	23.2	23.4	94.13	0.02861	22.8	22.5
98.10	0.02810	22.3	22.4				

FIG. 3.



ions, but as the concentration rises the proportion of colloid—both undissociated colloid and micelle—rises. McBain and his pupils

have brought forward considerable evidence to show that there is a definite equilibrium,



Their diagrams also indicate that the ratio of neutral colloid to micelle does not vary very greatly with the concentration. In the particular case of potassium oleate their work has given us considerable insight into the probable structure of the colloidal aggregates and it was hoped that the present experiments would throw some light on the breakdown of the complex.

An examination of the curves reveals the following features.

(i) The increase in density of the solutions over that of the mixed solvent remains practically constant until the composition 40–50 per cent. of alcohol is reached, when the curve rises rapidly and continues rising until the solution consists of pure alcohol. (ii) The increase of viscosity falls rapidly until the mixed solvent contains 10–15 per cent. of alcohol, when it becomes constant up to a composition of 40 per cent. of alcohol; the increase of viscosity produced by the colloid then falls rapidly to a minimum at 80 per cent. of alcohol, before rising slightly to the point representing pure alcohol. (iii) The curve showing the lowering of the surface tension sweeps down rather rapidly to the composition 40–50 per cent. of alcohol, when the lowering becomes practically zero, and remains so until the point representing pure alcohol is reached.

The change of slope of these curves occurs at practically the same ratio of water to alcohol for the two concentrations of oleate studied. This has been observed also in the case of viscosity maxima of colloidal solutions in mixed solvents by Masson and McColl (T., 1920, 117, 819).

The experimental data show three well-defined stages in the transition from water to alcohol. Thus, (i) from 0 to 45 per cent., the density effect is constant and almost negligible in magnitude, whilst in the complementary range from 45 to 100 per cent. the surface tension effect is negligible. The two phenomena thus agree in dividing the range of concentrations into two approximately equal sections, and in this they are in accord with the viscosity measurements, where a long period of constancy terminates at about 45 per cent. of alcohol. (ii) The viscosity curves, however, show a rapid drop from 0 to 10 per cent., which divides the range from 0 to 45 per cent. into two portions. The surface-tension curve in Fig. 3 rises to a maximum at much the same point and thus confirms the idea that a sub-division of the whole range into three parts is necessary.

The nature of the three stages in the breaking-down of the colloid is not yet clearly established. The surface-tension curves are perhaps the easiest to interpret, since it is clear that from 45 to 100 per cent. of alcohol there is no tendency for the soap to be adsorbed at the surface; its principal colloidal property has therefore disappeared. This may be taken to involve also the disappearance of the colloidal aggregate where a concentration of 45 per cent. of alcohol is reached. It remains to account for the initial stage in the breaking-down of the colloid, between 0 and 10 per cent., which produces no change of density, but causes a rapid fall of viscosity and a small rise of surface tension. It is suggested that this may be due either to a driving back of the electrolytic dissociation of the colloid, that is, to a return of the sodium ions to the micelle, or to an initial stage in the breaking-down of the micelle, but no conclusive argument can be used in favour of either of these hypotheses.

Summary.

(1) The density, viscosity, and surface tension of solutions of potassium oleate of two different concentrations in varying concentrations of water and alcohol from pure water to pure alcohol have been determined.

(2) The experimental results suggest that there are three stages in the breaking-down of the colloidal aggregate, extending over the ranges from 0—15, 15—45, and 45—100 per cent. of alcohol.

The author would like to express his gratitude to Professor T. M. Lowry for his interest in these experiments and for much valuable advice, and to the Department of Industrial and Scientific Research for a grant which has enabled this work to be done.

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[Received, December 20th, 1922.]

*XII. Studies in the n-Butyl Series. Part II. The Four Stereoisomeric $\beta\gamma$ -Di-*p*-tolylamino-*n*-butanes.*

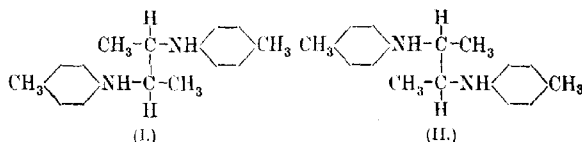
By GILBERT T. MORGAN and WILFRED JOHN HICKINBOTTOM.

IN the course of a study of *n*-butyl derivatives we have examined the reaction of the $\beta\gamma$ -dihalogenated *n*-butanes with ammonia and various primary amines. The chemical changes involved in these condensations are very complicated and so far the most definite results have been obtained with *p*-toluidine. The main product of the action of this aromatic base on $\beta\gamma$ -dichloro-*n*-butane or the

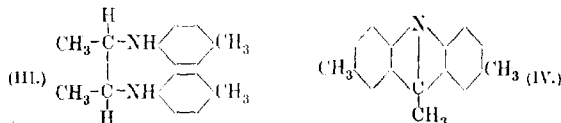
corresponding $\beta\gamma$ -dibromo-derivative is a mixture of $\beta\gamma$ -di-*p*-tolylamino-*n*-butanes, whereas the most readily recognisable by-product is 3 : 5 : 7-trimethylacridine (IV).

On isolating the foregoing diamines with the aid of their hydrochlorides and picrates it was found that two isomeric bases were obtained, one melting at 62–63° and the other at 57–58°.

The less fusible isomeride, which was resolved by means of *d*- α -bromocamphor- π -sulphonic acid into optically active dextro- and lævo-modifications, is accordingly the externally compensated dl- $\beta\gamma$ -di-*p*-tolylamino-*n*-butane (I and II).



The more fusible isomeride, which could not be resolved, is the internally compensated meso- $\beta\gamma$ -di-*p*-tolylamino-*n*-butane (III).



The four stereoisomeric $\beta\gamma$ -di-*p*-tolylamino-*n*-butanes demanded by theory have thus been obtained in a definitely crystalline form.

	M. p.	M_D^{20}
<i>dl</i> - $\beta\gamma$ -Di- <i>p</i> -tolylamino- <i>n</i> -butane	62–63	...
<i>d</i> - $\beta\gamma$ -Di- <i>p</i> -tolylamino- <i>n</i> -butane	87–88	268
<i>l</i> - $\beta\gamma$ -Di- <i>p</i> -tolylamino- <i>n</i> -butane	87–88	263
<i>meso</i> - $\beta\gamma$ -Di- <i>p</i> -tolylamino- <i>n</i> -butane	57–58	...

The *d*- and *l*-modifications crystallise in enantiomorphously related forms of the orthorhombic system and show no similarity to the *meso*-isomeride. The *dl*-form, on the other hand, is almost identical crystallographically with the active enantiomers, but it is not possible at present to state whether this is referable to a spontaneous resolution into an optically active conglomerate or to its occurrence in a pseudoracemoid condition. It is hoped to settle the question definitely as soon as a sufficient amount of material is available.

Prolonged heating of the hydrochlorides of the foregoing diamines in the presence of excess of *p*-toluidine leads to a decomposition of these bases with the production of 3 : 5 : 7-trimethylacridine (IV). The constitution of this acridine was determined by preparing the

base synthetically from acetaldehyde, *p*-toluidine, and *p*-toluidine hydrochloride. The two preparations gave identical products.

EXPERIMENTAL.

Preparation of $\beta\gamma$ -Dichloro-n-butane and $\beta\gamma$ -Libromo-n-butane.

The vapour of *n*-butyl alcohol * was passed through glacial phosphoric acid maintained at 300–350° in a cylindrical copper vessel, the resulting crude Δ^8 -butylene was cooled to room temperature and passed into a flask cooled in a freezing mixture, gaseous chlorine or liquid bromine being introduced into this absorption vessel at such a rate that only a slight excess of halogen was present throughout the operation. The crude butylene dihaloids were washed successively with aqueous alkali and water, dried, and distilled. The dichloride, fractionated several times to remove chlorinated products, was ultimately collected in the fraction 115.2–115.5°/752 mm. The dibromide was fractionated repeatedly until the purified product boiled at 157–158° under the ordinary pressure.

*Condensation of $\beta\gamma$ -Dichloro-n-butane and *p*-Toluidine.*

The dichlorobutane was heated with four to six molecular proportions of *p*-toluidine, the temperature being maintained at about 130–140°. After thirty hours, concentrated aqueous sodium carbonate was added and the excess of *p*-toluidine removed by distillation in steam. The dark, non-volatile residue was extracted with ether, the dried ethereal extract being distilled up to 290°. The fraction (A) collected between 200 and 290° was reserved for subsequent examination. The bulk of the condensation product which remained in the distillation flask was warmed with diluted hydrochloric acid, 40 c.c. of concentrated acid and 100 c.c. of water being used for 20 grams of the crude mixed bases. The dark, gummy mass on trituration changed into a hard, bulky, crystalline mass, which was recrystallised from boiling water. After separating a dark oil (B), the yellow, crystalline solid (C) was removed from the mother-liquor (D) and decomposed with aqueous sodium hydroxide, when a diamine separated as an oil which solidified on cooling. Crystallisation of this product from alcohol yielded the externally compensated base, dl- $\beta\gamma$ -di-*p*-tolylamino-*n*-butane. The alcoholic mother-liquor and the solution (D) gave further quantities of this base in the form of its picrate. The crude diamines, dissolved in benzene, were treated with a molecular proportion of picric acid, when on warming, the *dl*-picrate separated in bulky, orange-red crystals.

* The authors' thanks are due to Captain Desborough of the Royal Naval Cordite Factory for supplies of *n*-butyl alcohol.

The benzene mother-liquors of the *dl*-picrate yielded on addition of aqueous ammonia crude *meso-βγ-di-p-tolylamino-n-butane*, this base being purified by taking advantage of the slight solubility of its hydrochloride in absolute alcohol. The alcoholic solution of the crude diamine was evaporated to dryness with a slight excess of hydrochloric acid, and the residue extracted repeatedly with small quantities of warm absolute alcohol. The hydrochloride of the *meso*-diamine remained as a colourless powder.

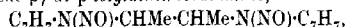
The dark oil (*B*) on extraction with ether left a dark brownish yellow solid (the acridine by-product), whilst the ethereal extract contained a further quantity of the *dl*- and *meso-βγ-di-p-tolylamino-n-butan*es. These mixed diamines were converted into hydrochlorides and the crude salts extracted with alcohol, when the *meso*-salt remained undissolved, whereas the mother-liquor contained the *dl*-isomeride and was worked up for this diamine together with the more soluble hydrochloride obtained from the mixed picrates.

The Externally Compensated Base, dl-βγ-Di-p-tolylamino-n-butane.—This diamine, obtained through its picrate, was set free by ammonia and purified by crystallising from alcohol; it separated in tabular, six-sided crystals, and melted at 62–63° (Found: C = 80.9; H = 9.4; N = 10.7. $C_{18}H_{24}N_2$ requires C = 80.54; H = 9.02; N = 10.44 per cent.).

The *dl-hydrochloride* crystallised from water or very dilute hydrochloric acid in hard, nodular crystals containing water of crystallisation (Found: N = 7.54; Cl = 18.77. $C_{18}H_{24}N_2 \cdot 2HCl \cdot 2H_2O$ requires N = 7.43; Cl = 18.80 per cent.). On drying at 100°, a rapid loss in weight of 9–10 per cent. occurred corresponding with elimination of the water, but longer drying led to a further loss, the residue being yellow and finally brown. After several days at 100°, the chlorine content had dropped to 17.24 per cent. and the total loss was 12.3 per cent.

The *dl-zincchloride*, precipitated as a white, curdy solid on mixing ethereal solutions of its generators, was hydrolysed by warm water (Found: Cl = 17.64. $C_{18}H_{24}N_2 \cdot ZnCl_2$ requires Cl = 17.53 per cent.). The *dl-picrate* separated from a benzene solution of picric acid and the diamine in orange-red, felted crystals, drying to a golden yellow colour and melting at 170° to a red liquid (Found: N = 14.19. $C_{18}H_{24}N_2 \cdot C_6H_3O_8N_3$ requires N = 14.08 per cent.). The picrate was only sparingly soluble in cold benzene, ether or light petroleum, dissolving more readily in ethyl acetate.

dl-Dibenzoyl-βγ-di-p-tolylamino-n-butane crystallised from alcohol in prisms melting at 214° (Found: N = 6.29. $C_{32}H_{32}O_2N_2$ requires N = 5.88 per cent.).

dl-n-Butylene-βγ-di-p-tolyldinitrosodiamine,

prepared by adding aqueous sodium nitrite to the diamine, dissolved in 50 per cent. acetic acid, was precipitated by ether and crystallised from light petroleum in tabular crystals melting at 88–89°; it responded to the Liebermann test (Found: N = 17.42. $\text{C}_{18}\text{H}_{22}\text{O}_2\text{N}_4$ requires N = 17.17 per cent.).

The *tetrahydroglyoxaline* derivative of the *dl*-diamine was obtained by warming an alcoholic solution of this base with 30 per cent. neutral formaldehyde solution. On cooling, the product separated and was recrystallised from alcohol in tabular forms melting at 107–108° (Found: N = 10.28. $\text{C}_{10}\text{H}_{24}\text{N}_2$ requires N = 10.00 per cent.). This tetrahydroglyoxaline was soluble in the ordinary organic media; its picrate crystallised from benzene in clusters of bright yellow needles melting at 137°.

Resolution of dl-βγ-di-p-tolylamino-n-butane.

Preliminary experiments with Reychler's camphorsulphonic acid failed to produce any resolution; the *d*-camphorsulphonate separated in prismatic needles melting at 222° with effervescence, and no appreciable separation was observable after repeated crystallisations from dilute alcohol. The resolution was, however, effected by adding 5.3 grams of *d*-*z*-bromocamphor-*π*-sulphonic acid in 18.5 c.c. of water to the externally compensated base (2.1 grams), dissolved in a small amount of ether. A viscous, semi-solid mass resulted which on warming with more ether became harder and more crystalline. The precipitate was washed repeatedly with ether until quite hard; the residue then weighed 3.3 grams. After one crystallisation from alcohol this salt was decomposed with dilute aqueous ammonia and the liberated diamine separated by extraction with ether.

dextro-βγ-di-p-tolylamino-n-butane (formula I) separated from alcohol in hard, colourless tablets melting at 87–88°; it was more sparingly soluble in alcohol and light petroleum than the *dl*-base (Found: C = 80.6; H = 9.1; N = 10.5. $\text{C}_{18}\text{H}_{24}\text{N}_2$ requires C = 80.54; H = 9.02; N = 10.44 per cent.). A determination of its optical activity in commercial absolute alcohol ($c = 3.35$) gave $[\alpha]_D^{20} + 100^\circ$, whence $[\text{M}]_D^{20} + 268^\circ$.

The *d-hydrochloride* separated from water containing a little hydrochloric acid in slender, anhydrous needles (Found: Cl = 20.8. $\text{C}_{18}\text{H}_{24}\text{N}_2\cdot 2\text{HCl}$ requires Cl = 20.78 per cent.).

levo-βγ-di-p-tolylamino-n-butane (formula II) was isolated from the more soluble portions of the *d*-*z*-bromocamphor-*π*-sulphonate by decomposing this salt with dilute ammonia; the diamine was crystallised repeatedly from light petroleum and absolute alcohol.

It separated from the latter solvent in tablets melting at 87–88° (Found: C = 80.65; H = 9.15; N = 10.6. $C_{18}H_{24}N_2$ requires C = 80.54; H = 9.02; N = 10.44 per cent.). A determination of optical activity in commercial absolute alcohol ($c = 3.33$) gave $[\alpha]_D^{25} = 98^\circ$, whence $[M]_D^{25} = 263^\circ$.

The *l*-hydrochloride separated from very dilute hydrochloric acid in colourless, slender needles (Found: Cl = 20.82. $C_{18}H_{24}N_2 \cdot 2HCl$ requires Cl = 20.78 per cent.).

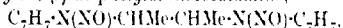
Equal weights of the *d*- and *l*-diamines, when mixed and dissolved in alcohol, yielded the *dl*-base on concentration of the solvent.

meso- $\beta\gamma$ -*Di*-*p*-tolylamino-*n*-butane (Formula III).—This diamine, which was obtained from the hydrochloride remaining insoluble after extraction with absolute alcohol, showed at first no tendency to solidify, but was finally obtained crystalline by inoculation with a fragment of solid obtained by cooling a portion of the amine to -15° in the presence of light petroleum. The *meso*-diamine separated from light petroleum in tabular crystals melting at 57–58° (Found: C = 80.9; H = 9.2; N = 10.6. $C_{18}H_{24}N_2$ requires C = 80.54; H = 9.02; N = 10.44 per cent.).

The *meso*-diamine was more soluble in organic solvents than the externally compensated base. Unlike the latter, it gave a *d*- α -bromocamphor- π -sulphonate which remained homogeneous after repeated crystallisation from aqueous alcohol.

The *meso*-hydrochloride crystallised from aqueous alcohol in prismatic needles melting at 229–230° (Found: N = 8.46; Cl = 20.75. $C_{18}H_{24}N_2 \cdot 2HCl$ requires N = 8.21; Cl = 20.78 per cent.). The *meso*-dibenzoyl derivative separated from alcohol in small, white crystals melting at 193–194° (Found: N = 5.7. $C_{32}H_{32}O_2N_2$ requires N = 5.88 per cent.).

meso-*n*-Butylene- $\beta\gamma$ -*di*-*p*-tolyl dinitrosodiamine,



prepared by adding sodium nitrite to the *meso*-diamine, dissolved in 50 per cent. acetic acid, crystallised from warm methyl alcohol in iridescent tablets having a slight buff tint; it melted at 146–147° (Found: N = 17.48. $C_{18}H_{22}O_2N_4$ requires N = 17.47 per cent.). The *meso*-dinitrosodiamine was distinguished from its *dl*-isomeride in being less soluble in methyl alcohol, and may be isolated from a mixture of the two by crystallisation from this solvent.

On adding concentrated hydrochloric acid to the dinitrosodiamine (1.1 grams) dissolved in 15 c.c. of glacial acetic acid on the water-bath, effervescence occurred with evolution of brown fumes. The heating was continued until the action had ceased, when the solution was diluted with water and extracted with benzene to remove tar. *meso*- $\beta\gamma$ -*Di*-*p*-tolylamino-*n*-butane was liberated from the acid solu-

tion by adding sodium hydroxide and extracting with ether, and was converted into its sparingly soluble hydrochloride (0.35 gram). The low yield was probably due to oxidation during the liberation of nitrous acid; the product was, however, *meso*-diamine identical with that isolated from the condensation between butylene dichloride and *p*-toluidine.

The *tetrahydroglyoxaline* of the *meso*-diamine separated in thin plates or laminae on mixing an alcoholic solution of the base with aqueous formaldehyde. After crystallisation from alcohol this compound was obtained in colourless needles melting at 94° (Found: $N = 10.19$. $C_{19}H_{24}N_2$ requires $N = 10.0$ per cent.).

The *By-product*, 3:5:7-Trimethylacridine (Formula IV).—The dark oil *B* (p. 99), when extracted with benzene and ether to remove the isomeric diamines, left a dark solid residue of a *hydrochloride*. This residue, when purified by repeated crystallisation from hot water, separated in felted masses of bright yellow, hydrated needles sparingly soluble in cold water. On drying, this hydrochloride lost 17.2 per cent. of water, and the residue gave $Cl = 13.65$, 13.33. $C_{16}H_{15}N \cdot HCl \cdot 3H_2O$ requires $H_2O = 17.3$. $C_{16}H_{15}N \cdot HCl$ requires $Cl = 13.76$ per cent. A dilute aqueous solution of this hydrochloride showed an intense green fluorescence. 3:5:7-Trimethylacridine, obtained as a white, flocculent mass by adding ammonia to the yellow hydrochloride, was dried, and crystallised from light petroleum (b. p. 80 – 100°) in long, pale yellow needles melting at 133 – 134° ; by slow crystallisation, well-formed, amber crystals separated [Found: $C = 87.2$; $H = 7.1$; $N = 6.6$. $M = 221$ in benzene by freezing point ($c = 2.06$). $C_{16}H_{15}N$ requires $C = 86.9$; $H = 6.8$; $N = 6.3$ per cent.; $M = 221$]. The colourless needles of 3:5:7-trimethylacridine contained water of crystallisation: on drying in a vacuum desiccator, they become opaque and fall to powder.

The *iodide* separated from boiling water in orange-red, anhydrous needles sparingly soluble in hot water (Found: $I = 36.38$. $C_{16}H_{15}N \cdot HI$ requires $I = 36.35$ per cent.).

The *perchlorate* formed light yellow crystals sparingly soluble in cold water; its dilute alcoholic solution showed an intense green fluorescence. The *dichromate* was a bulky, yellow precipitate, and the *picrate* a bright yellow, sparingly soluble powder melting at 225 – 226° .

3:5:7-Trimethylacridine *nitrate* separates from warm water in small, yellow needles (Found: $N = 10.26$. $C_{16}H_{15}N \cdot HNO_3$ requires $N = 9.86$ per cent.).

3:5:7-Trimethylacridinium *methyl iodide*, prepared by warming the acridine with an excess of methyl iodide, crystallises from warm water in slender, scarlet needles (Found: $I = 34.58$. $C_{17}H_{18}NI$

requires $I = 34.95$ per cent.). It is not readily soluble in cold absolute alcohol or water, but is more soluble on warming. A dilute aqueous solution, when treated with a dilute solution of sodium hydroxide, rapidly yielded a greenish turbidity, which gradually became white.

3:5:7-Trimethylacridine was synthesised in small yield by adding 6 c.c. of acetaldehyde to 10 grams of purified *p*-toluidine, the solution being warmed on the water-bath until it became dark red. Fifteen grams of *p*-toluidine and 9 c.c. of concentrated hydrochloric acid were added, the mixture was heated on the sand-bath for nine hours, and then poured into excess of dilute hydrochloric acid. The precipitate was recrystallised from hot water and after two crystallisations 0.35 gram of air-dried 3:5:7-trimethylacridine hydrochloride was obtained (Found: $H_2O = 17.65$ per cent.). A portion was converted into iodide (Found: $I = 36.40$, $C_{16}H_{15}N, HI$ requires $I = 36.35$ per cent.). The base, liberated from its salts and recrystallised from light petroleum, melted at 133° and was identical with the foregoing product.

*Conversion of $\beta\gamma$ -Di-*p*-tolylamino-*n*-butane into 3:5:7-Trimethylacridine.*—The hydrochloride of *dl*- $\beta\gamma$ -di-*p*-tolylaminobutane, when heated in an open tube for twenty-five hours, gave a white sublimate which subsequently darkened. The product was then rendered alkaline and distilled in steam, when *p*-toluidine was identified among the volatile products. Trimethylacridine was not detected among the non-volatile products. When the hydrochloride from 5 grams of *dl*-diamine was heated with 8 grams of *p*-toluidine in an open tube at $180-220^\circ$ for forty hours, a small amount of secondary base was identified among the products volatile in steam. From the non-volatile residue 1 gram of trimethylacridine hydrochloride was isolated and further amounts were recovered in the form of picrate. The non-volatile residue insoluble in dilute hydrochloric acid was identified as di-*p*-tolylamine.

*Notes on the Reaction between the $\beta\gamma$ -Dihalogenated *n*-Butanes and *p*-Toluidine.*

In repeated condensations it was found that the yield of $\beta\gamma$ -di-*p*-tolylamino-*n*-butanes diminished when either the reaction was prolonged or the temperature was too high. Fifty grams of $\beta\gamma$ -dichloro-*n*-butane and 200 grams of *p*-toluidine heated for forty hours at $140-150^\circ$ furnished 27 grams of the *dl*-diamine, 11 grams of the *meso*-diamine, and 1 gram of 3:5:7-trimethylacridine. When the time was prolonged to sixty hours, the yield of diamines decreased and the amount of 3:5:7-trimethylacridine rose to 7 grams. At $180-220^\circ$ for forty hours, the diamines disappeared and the only

recognisable products were 3:5:7-trimethylacridin¹ and di-*p*-tolylamine (m. p. 79°; nitrosoamine, m. p. 101—103°).

β-γ-Dibromo-*n*-butane reacted with *p*-toluidine in a similar manner but more readily, so that it is unnecessary to give details of the condensation.

The more volatile by-products (fraction *A*, p. 99) contain monoamines produced by the interaction of *p*-toluidine and the dihalogenated *n*-butanes in molecular proportions; these substances are under examination together with the products of the action of ammonia and other bases on the dihalogenated butanes.

The authors desire to express their thanks to the Department of Scientific and Industrial Research for grants which have partly defrayed the expense of this investigation.

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[Received, December 13th, 1922.]

XIII.—*Investigations on the Dependence of Rotatory Power on Chemical Constitution. Part XVIII.** *The Di-1-menthyl Esters of the Saturated Dicarboxylic Acids.*

By LESLIE HALL.

It has been shown in the earlier parts of these investigations, and particularly in Part XIII, that the rotatory powers of those members of a homologous series containing within the molecule a chain of five (or a multiple of five) carbon (or carbon and oxygen) atoms frequently deviate considerably from what may be considered to be the normal values for such compounds. In Part XVI, however, a homologous series of optically active esters of dibasic acids is described in which this effect is subordinated to, and almost obliterated by, an alternating effect due possibly to the alternate *cis*- and *trans*-structure of the saturated dicarboxylic acids and their derivatives. In the latter investigation, too, it was shown, as was perhaps to be expected, that the optically active esters of the dibasic acids exhibit complex rotatory dispersion which persists over a wider range of experimental conditions than does the complex rotatory dispersion shown by the corresponding esters of the monobasic acids. This effect can be attributed to the fact that in

* In this paper references are made to Part XIII, this vol., p. 1, and to Part XVI, *ibid.*, p. 32.

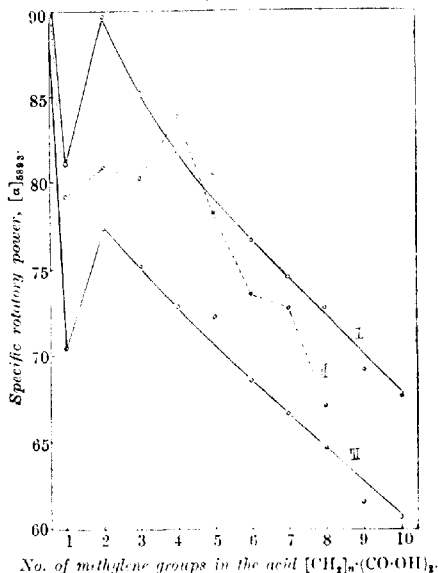
the former case there are two centres of possible dynamic isomerism—carboalkyloxy groups—in the molecule, whilst in the latter case there is only one.

In view of these facts, then, it was considered of interest to extend the scope of the investigation to include another similar series of dibasic esters with a different alcohol as the source of optical

FIG. 1.

The specific rotatory powers, $[\alpha]_{589}^{25}$, of the dibasic esters of l-menthol.

- I. In 5% chloroform solution.
- II. Ditto. Values given by Hilditch.
- III. In the homogeneous state at 80°.



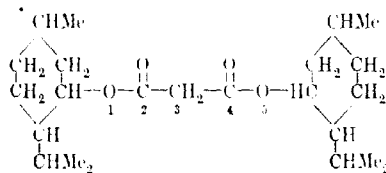
activity. Such a series has already been described by Hilditch (T., 1909, 95, 1581), and his results show an abnormal value for the rotatory power of the adipic member which cannot be explained by any theory put forward in this series of investigations. In view of the conclusions summarised in Part XIII, it was thought that this abnormality might reappear, perhaps in a modified form, at that member of the series containing five more carbon atoms than the adipate, and, in order not only to render the results comparative, but also to carry out measurements of rotatory

dispersion, it was decided to synthesise the whole series afresh from the oxalate to the *n*-decane- α -dicarboxylate.

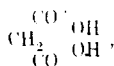
The results of this investigation show that the abnormal value of the rotatory power of the adipic ester found by Hilditch has no real existence; that, within the limits of experimental error, the series shows a regular variation of rotatory power from member to member, except in the case of the oxalate and the malonate and possibly with slight irregularities in the cases of the esters of the acids containing five and nine methylene groups; and that the esters all exhibit simple rotatory dispersion under all the experimental conditions studied.

Fig. 1 shows, *inter alia*, the comparison between the results obtained by Hilditch and those obtained in this investigation. It will be seen that in every case except one the rotatory powers of the esters now described are considerably higher than those recorded by Hilditch, which is in itself strong evidence of the optical purity of these esters. In the one remaining case, it is found that the melting point of the ester of lower rotation now described is higher than that of the corresponding ester prepared by Hilditch, thus indicating a state of higher chemical purity in the specimen prepared in the course of this investigation. The high rotatory power exhibited by the oxalate has its parallel in the case of the di-*d*- β -octyl oxalate (Part XVI) and perhaps also in the abnormally low rotatory powers exhibited by the alkyl formates (Part XIII), the corresponding first members of the series of monobasic esters.

The low rotatory power of the malonate is possibly due to the chain of three carbon and two oxygen atoms connecting the hydro-aromatic rings.



A *cis*-configuration has already been assigned to malonic acid by Price and Brazier (T., 1915, 107, 1719) and it will readily be seen that this formulation,



is by no means inconsistent with that adopted in this and earlier parts of this investigation to account for irregularities in the

rotatory power of those members of a homologous series which contain a complete chain of $5 \times n$ atoms of carbon or of carbon and oxygen.

That the suberic ester does not show any irregularity of rotatory power as compared with the rotatory powers of the other members of the series is perhaps due to the fact that, although it possesses a chain of eight carbon atoms and two oxygen atoms connecting the hydroaromatic rings, this ester must be considered to possess a *trans*-structure and so the development of the spiral form of the chain is prevented. It should be pointed out, however, that no irregularity can be detected in the rotatory power of di-*d*- β -octyl azelate (Part XVI), although this ester should possess a *cis*-configuration and contains five more carbon atoms than di-*d*- β -octyl succinate, which possesses a low rotatory power.

If the molecular rotatory powers of the esters be calculated, it will be seen that after the first three members they tend to a constant value, this being in accordance with Tschugaev's rule. A similar result is to be found in the case of the di- β -octyl esters described in Part XVI.

It is noteworthy that these esters exhibit simple rotatory dispersion in that the variation of rotatory power with the wave-length of the light used can be expressed by a Drude equation with one term. This was tested by the simple expedient of plotting the reciprocal of the rotatory power against the square of the wave-length, when linear curves were obtained. As, however, only three points were available for each ester, it was considered advisable to extend the observations, and accordingly the rotatory power of the sebacic ester was determined by a photographic method for radiations of shorter wave-length, using the iron arc as illuminant. Five additional readings were thus obtained and it was then found that the eight values of the rotatory power of this ester for radiations of wave-lengths between $\lambda = 5893$ and $\lambda = 3767$ could be expressed by a Drude equation with one term.

It is also of interest to note that the specific rotatory powers of these esters are influenced only slightly by change of temperature. They are therefore very different from the corresponding esters of *d*- β -octanol, the rotations of which possess a considerable temperature coefficient.

EXPERIMENTAL.

The *L*-menthol used throughout these experiments was specially pure material obtained from Schimmel, and possessed $[\alpha]_D^{20} = -49.46$ in 5 per cent. ethyl alcoholic solution.

The esters, with the exception of the malonate, were prepared

by the method described by Hilditch (*loc. cit.*), that is, the pure acid chloride was mixed with a slight excess of menthol, and the mixture heated at 100° for four or five hours until the evolution of hydrogen chloride had ceased. The product was dissolved in ether, washed carefully with dilute aqueous sodium carbonate solution to remove traces of acids, and then distilled in steam to remove excess of menthol, it being found that the esters were unaffected by such treatment. The non-volatile residue of ester was extracted with ether, dried over potassium carbonate, and fractionally distilled under reduced pressure.

l-Menthyl Malonate.—This ester was prepared by heating *l*-menthol (10 grams) with malonic acid (3 grams) and three drops of strong sulphuric acid at 110° for fifteen hours. The dark-coloured product was dissolved in ether, washed with dilute sodium carbonate solution, and purified as described above.

The esters were obtained either as very faintly odorous, crystalline solids or as very viscous, odourless liquids. They were found to have the following melting and boiling points: Di-*l*-menthyl malonate, m. p. $61-62^{\circ}$, b. p. $169-170^{\circ}/1$ mm.; succinate, m. p. 63° , b. p. $200-205^{\circ}/2$ mm.; glutarate, m. p. $45-46^{\circ}$, b. p. $180-183^{\circ}/1$ mm.; adipate, m. p. $63-64^{\circ}$, b. p. $190-194^{\circ}/1$ mm.; pimelate, m. p. 45° , b. p. $216-217^{\circ}/2$ mm.; suberate, m. p. $36-37^{\circ}$, b. p. $205-208^{\circ}/1$ mm.; azelate, b. p. $225-228^{\circ}/2$ mm.; sebacate, b. p. $216-217^{\circ}/1$ mm.; *n*-nonane- α -dicarboxylate, b. p. $235-238^{\circ}/3$ mm.; *n*-decane- α -dicarboxylate, b. p. $225-228^{\circ}/2$ mm.

The specimen of the pimelic ester, in contrast to that described by Hilditch, boils without decomposition at 2 mm. pressure and shows no tendency to resinify on keeping.

In the case of the esters which are liquid at the ordinary temperature, density determinations were carried out using a carefully calibrated pycnometer holding about 1.5 c.c. at temperatures ranging from 20° to 100° . The densities of the solid esters were determined at temperatures extending from their melting points to 130° .

Observations of rotatory power in the homogeneous state were made using a jacketed 50 mm. tube, round which hot oil was circulated. The light of the sodium flame and of the mercury are used for these determinations. The rotatory power of each of the esters was also observed using pure chloroform as a solvent. The same sample of the freshly purified solvent was used throughout the experiments. In every case the rotatory power was observed using a 2-dm. tube, the concentration of the ester in the solution being approximately 5 per cent.

The rotatory powers of the esters were found to be unaffected

by distillation under reduced pressure and by heating at atmospheric pressure to 140°. The *l*-menthol obtained by hydrolysing samples of each of the esters was found to possess its maximum rotatory power.

TABLE I.

Observations of Density, D_4^{20} , and Rotatory Power in the Homogeneous State.

Rotations are here given as for a 1-dm. tube and are all negative in sign.

The values for the rotatory power of *l*-menthyl oxalate in the homogeneous state are not here reproduced, as they have already been published (Kenyon and Pickard, T., 1915, **107**, 35).

l-Menthyl malonate.

D_4^{20} 0.9443 at 76°; 0.9292 at 95.5°; 0.9149 at 112.5°; 0.9026 at 127.5°.
 α_{5893} 66.78° at 69°; 65.64° at 92°; 64.76° at 112°; 63.90° at 129°.
 α_{5461} 77.94° at 70°; 76.54° at 93°; 75.86° at 112°; 75.04° at 129°.
 α_{4368} 128.50° at 69°; 126.68° at 93°; 125.26° at 112°; 124.06° at 129°.

l-Menthyl succinate.

D_4^{20} 0.9469 at 71°; 0.9249 at 97°; 0.9111 at 114.5°; 0.9038 at 124.5°.
 α_{5893} 72.42° at 85°; 71.76° at 99.5°; 71.30° at 120°; 70.10° at 139°.
 α_{5161} 84.28° at 84°; 83.72° at 100°; 83.28° at 119°; 82.50° at 139°.
 α_{4358} 139.70° at 84°; 139.04° at 100°; 137.74° at 120°; 136.52° at 139°.

l-Menthyl glutarate.

D_4^{20} 0.9491 at 60°; 0.9396 at 74°; 0.9313 at 83°; 0.9170 at 101°.
 α_{5893} 71.50° at 61°; 70.04° at 84°; 69.16° at 101°; 68.14° at 117°; 67.14° at 134°.
 α_{5461} 83.06° at 62°; 82.34° at 85°; 81.14° at 102°; 80.14° at 117°; 78.74° at 134°.
 α_{4358} 140.56° at 61°; 137.30° at 85°; 135.44° at 101°; 133.64° at 117°; 131.64° at 134°.

l-Menthyl adipate.

D_4^{20} 0.9337 at 74.5°; 0.9196 at 91.5°; 0.9059 at 110.5°; 0.8939 at 125.5°.
 α_{5893} 67.76° at 79°; 66.34° at 106°; 65.42° at 118°; 64.06° at 142°.
 α_{5461} 79.14° at 78°; 77.72° at 100°; 76.84° at 118°; 75.34° at 143°.
 α_{4358} 132.44° at 78°; 130.12° at 100°; 127.96° at 118°; 125.68° at 142°.

l-Menthyl pimelate.

D_4^{20} 0.9479 at 51°; 0.9361 at 65.5°; 0.9253 at 80°; 0.9082 at 101°.
 α_{5893} 68.32° at 60°; 66.78° at 80°; 65.76° at 98°; 64.38° at 120°; 62.82° at 141°.
 α_{5461} 79.88° at 61°; 77.88° at 81°; 76.74° at 99°; 75.48° at 120°; 74.10° at 141°.
 α_{4358} 132.74° at 61°; 130.05° at 80°; 128.26° at 98°; 125.66° at 120°; 123.60° at 141°.

TABLE I.—(continued).

l-Menthyl suberate.

D_4^0 0.9432 at 50.5°; 0.9337 at 63.5°; 0.9213 at 80°; 0.9059 at 101°.
 α_{5895} 64.74° at 56°; 63.16° at 78°; 62.18° at 99°; 61.38° at 118°; 60.46° at 137°.
 α_{5461} 76.28° at 57°; 74.40° at 79°; 73.32° at 99°; 72.38° at 118°; 71.34° at 138°.
 α_{4358} 127.08° at 56°; 124.32° at 79°; 122.52° at 99°; 120.48° at 118°; 118.68° at 137°.

l-Menthyl azelate.

D_4^0 0.9557 at 29°; 0.9399 at 50.5°; 0.9266 at 70°; 0.9040 at 100.5°.
 α_{5895} 64.64° at 16°; 63.62° at 35.5°; 62.50° at 57°; 61.18° at 81°; 60.46° at 95°; 59.62° at 115°; 58.68° at 132°.
 α_{5461} 76.24° at 16°; 75.18° at 35°; 73.38° at 57°; 71.84° at 81°; 70.94° at 95°; 69.94° at 115°; 69.34° at 132°.
 α_{4358} 126.18° at 16°; 124.16° at 35°; 121.70° at 57°; 119.30° at 81°; 118.38° at 94°; 116.46° at 112°; 114.94° at 132°.

l-Menthyl sebacate.

D_4^0 0.9477 at 31.5°; 0.9356 at 49°; 0.9226 at 68°; 0.8974 at 101°.
 α_{5895} 61.92° at 19°; 60.38° at 45°; 59.66° at 65°; 58.72° at 88°; 57.96° at 108°; 56.94° at 127°; 56.24° at 140°.
 α_{5461} 73.12° at 19°; 71.20° at 45°; 69.98° at 65°; 68.60° at 89°; 67.60° at 109°; 66.66° at 128°; 65.86° at 141°.
 α_{4358} 120.84° at 19°; 116.42° at 45°; 115.48° at 65°; 114.04° at 89°; 112.68° at 109°; 110.72° at 128°; 110.00° at 141°.

The following photographic observations were recorded for a 1-dm. tube at 17°.

$$\alpha_{4361} = 130.0^\circ; \alpha_{4358} = 139.7^\circ; \alpha_{5998} = 150.0^\circ; \alpha_{5887} = 160.0^\circ; \alpha_{5767} = 169.6^\circ;$$

whence

$$[\alpha]_A^{17} \text{ for } \lambda_{4281} = 135.7^\circ; \lambda_{4045} = 145.8^\circ; \lambda_{3898} = 156.6^\circ; \lambda_{3887} = 167.0^\circ; \lambda_{3767} = 177.0^\circ.$$

l-Menthyl *n*-nonane- α -dicarboxylate.

D_4^0 0.9445 at 30.5°; 0.9305 at 48.5°; 0.9164 at 60°; 0.8925 at 100.5°.
 α_{5895} 59.36° at 21°; 57.02° at 54°; 56.02° at 80°; 54.94° at 105°.
 α_{5461} 70.00° at 21°; 65.60° at 55°; 63.96° at 79°; 62.84° at 105°.
 α_{4358} 115.86° at 21°; 110.96° at 55°; 108.92° at 79°; 106.20° at 105°.

l-Menthyl *n*-decane- α -dicarboxylate.

D_4^0 0.9445 at 29°; 0.9292 at 50°; 0.9164 at 69.5°; 0.8923 at 100.5°.
 α_{5895} 58.64° at 17.5°; 56.32° at 53°; 55.04° at 80.5°; 53.98° at 103.5°.
 α_{5461} 68.26° at 17.5°; 63.72° at 53°; 62.22° at 80.5°; 60.92° at 103°.
 α_{4358} 113.46° at 17.5°; 108.42° at 53°; 106.10° at 80.5°.

TABLE II.

Rotatory Powers of Esters at Different Temperatures.

<i>l</i> -Menthyl malonate.					<i>l</i> -Menthyl succinate.				
t° .	D_4^0 .	$[\alpha]_{5895}$.	$[\alpha]_{5461}$.	$[\alpha]_{4358}$.	t° .	D_4^0 .	$[\alpha]_{5895}$.	$[\alpha]_{5461}$.	$[\alpha]_{4358}$.
80°	0.9408	-70.39°	-82.12°	-135.6°	80°	0.9393°	-77.32°	-89.86°	-149.1
100	0.9248	-70.66	-82.43	-136.2	100	0.9229	-77.60	-90.63	-150.2
120	0.9087	-70.87	-83.03	-137.1	120	0.9064	-78.59	-91.77	-151.7

TABLE II.—(continued).

<i>l</i> -Menthyl glutarate.					<i>l</i> -Menthyl adipate.				
60	0.9491	75.37	88.57	148.1	80	0.9262	72.74	85.02	142.2
80	0.9334	75.19	88.47	147.8	100	0.9137	72.52	85.07	142.2
100	0.9177	75.18	88.41	147.7	120	0.8982	72.57	85.35	142.2
120	0.9021	75.41	88.57	147.7					
<i>l</i> -Menthyl pimelate.					<i>l</i> -Menthyl suberate.				
60	0.9406	72.59	85.00	141.2	60	0.9362	68.80	81.17	135.2
80	0.9248	72.23	84.37	140.7	80	0.9213	68.50	80.79	135.0
100	0.9089	72.13	84.37	140.7	100	0.9065	68.52	80.83	135.1
120	0.8927	72.14	84.57	140.8	120	0.8915	68.71	80.97	135.1
<i>l</i> -Menthyl azelate.					<i>l</i> -Menthyl sebacate.				
20	0.9618	66.92	78.93	130.8	20	0.9562	64.68	76.37	126.1
40	0.9476	66.85	78.61	130.4	40	0.9417	64.55	76.00	125.5
60	0.9333	66.70	78.39	130.1	60	0.9273	64.55	75.77	125.3
80	0.9189	66.64	78.18	129.8	80	0.9128	64.66	75.70	125.5
100	0.9044	66.65	78.12	129.8	100	0.8980	64.79	75.77	126.1
120	0.8900	66.74	78.34	130.1	120	0.8831	65.03	75.97	126.5
<i>l</i> -Menthyl <i>n</i> -nonane- α -dicarboxylate.					<i>l</i> -Menthyl <i>n</i> -decane- α -dicarboxylate.				
20	0.9522	62.30	73.60	121.8	20	0.9508	61.42	71.36	118.9
40	0.9374	61.66	71.74	120.5	40	0.9364	60.87	69.66	117.4
60	0.9227	61.53	70.68	119.7	60	0.9219	60.66	68.82	116.9
80	0.9079	61.58	70.50	119.6	80	0.9073	60.63	68.55	116.9
100	0.8932	61.83	70.53	119.7	100	0.8924	60.68	68.47	

TABLE III.

Table of Rotations of Esters in Chloroform Solution.

In these experiments, about 1 gram of the ester was made up to 20 c.c. with pure chloroform at the temperature of the laboratory. Rotations were then determined at that temperature using a 2-dm tube.

Name of ester.	Wt. of ester in 100 c.c. of solution.	$\alpha_{589\text{m}}$	$\alpha_{516\text{m}}$	$\alpha_{435\text{m}}$	$[\alpha]_{589\text{m}}^{20}$	$[\alpha]_{516\text{m}}^{20}$	$[\alpha]_{435\text{m}}^{20}$
<i>l</i> -Menthyl							
oxalate	4.82	-10.11	-12.01	20.15	104.8	124.6	209.0
malonate	4.98	8.07	9.32	15.53	81.12	93.67	156.1
succinate	5.19	9.30	10.88	18.21	89.68	104.8	175.6
glutarate	4.95	8.32	9.82	16.26	84.12	99.28	164.4
adipate	5.04	8.23	9.52	15.93	81.75	94.56	158.2
pimelate	4.96	7.95	9.09	15.32	80.56	92.10	155.2
suberate	4.71	7.21	8.41	14.04	76.58	89.33	149.1
azelate	5.10	7.60	8.81	14.77	74.44	86.30	144.6
sebacate	5.02	7.30	8.32	14.06	72.74	82.90	140.1
<i>n</i> -nonane- α -dicarboxylate	5.00	6.90	8.13	13.64	69.05	81.47	136.4
<i>n</i> -decane- α -dicarboxylate	5.01	6.78	7.90	13.20	67.67	78.84	131.7

Part of the expense involved in this investigation was defrayed by a grant from the Government Grant Committee of the Royal Society.

The author wishes to express his thanks to the Department of Scientific and Industrial Research for a personal grant which enabled this work to be carried out, to Dr. Kenyon for his interest and help, and to Mr. H. Hunter for carrying out the photographic observations of rotatory power.

BATTERSEA POLYTECHNIC, S.W. 11.

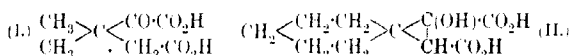
[Received, December 20th, 1922.]

XIV.—*Ring-chain Tautomerism. Part IV. The Effect of the Methyl Ethyl Grouping on the Carbon Tetrahedral Angle.*

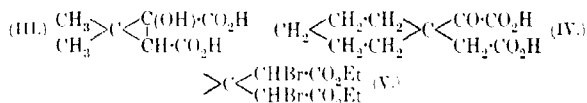
By BALBIR SINGH and JOCELYN FIELD THORPE.

THE recent experiments of Deshapande and Thorpe (T., 1922, **121**, 1430) on $\beta\beta$ -diethylglutaric acid have shown that, in accordance with the general hypothesis regarding the influence of groups on the depression of the tetrahedral angle, the effect produced by the *gem*-diethyl grouping lies approximately midway between those caused by the *gem*-dimethyl group and by the six-carbon ring.

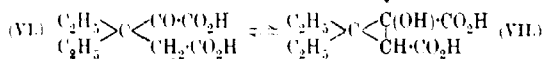
On the other hand, attention was directed to the very marked differences in chemical behaviour which accompanied the comparatively small alteration in angle, and particularly as regards the stability of the open-chain or ring system which was the outcome of the change. Thus, whereas the keto-acid (I) is the stable form in the dimethyl series, the ring hydroxy-acid (II) is the stable



structure in the six-ring series, and, as a matter of fact, so much is this the case that it has not been found possible to prepare the ring hydroxy-acid (III) or the keto-acid (IV) in spite of the fact that the

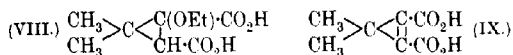


starting point was in each case the dibromo-ester (type V) or the corresponding bromo-lactone. These results were, however, brought into line by the discovery by Deshapande and Thorpe that the keto-acid (VI) and the hydroxy-ring acid (VII) in the diethyl



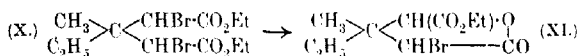
series were tautomeric. That is to say, they were mutually interconvertible in strong potash solution; a discovery which again emphasised the wide chemical differences produced by a slight angle alteration, because the keto-acid (I) and the hydroxy-ring acid (II) are unaltered by alkali.

There are, moreover, other points of difference which reveal themselves when the experimental data derived from the three series (dimethyl, diethyl, and *cyclohexane*) are compared. For example, when the hydrolysis of the dibromo-ester of type V is carried out with ethyl alcoholic potash, the products in the cases of the diethyl and *cyclohexane* series are the same as with aqueous potassium hydroxide, whereas in the dimethyl series the sole product is the ethoxy-derivative (VIII) and no trace of the keto-acid is produced. This remarkable reaction was considered by Perkin and Thorpe (T., 1901, **79**, 729) to be due to the addition of alcohol to the unsaturated compound (IX). It is evident that this

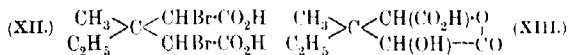


fundamental difference between the dimethyl and diethyl series must rest on the small difference of angle in the two series, and in order to study the effect produced by diminishing this difference we have carried out a series of comparative experiments in the methyl ethyl series.

$\beta\beta$ -Methylethylglutaric acid is readily prepared from methyl ethyl ketone by the Guareschi method. The anhydride dibrominates normally, but the dibromo-ester (X) loses ethyl bromide when distilled, and passes into the bromo-lactonic ester (XI) (compare Beasley, Ingold, and Thorpe, T., 1915, **107**, 1080).

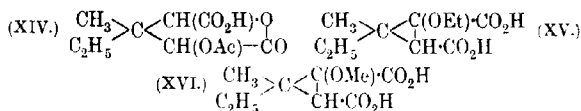


The dibromo-acid (XII) was isolated in *cis*- and *trans*-forms, both of which gave the same hydroxylactonic acid (XIII) with sodium carbonate. Like the corresponding lactonic acid in the diethyl



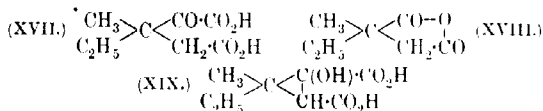
series, the acid (XIII) is unaltered by strong aqueous caustic alkali, and there is thus no tautomerism between the hydroxylactone-hydroxy-ring acid and keto-acid such as was shown to be the case with Balbiano's acid (Kon, Stevenson, and Thorpe, T., 1922, **121**, 650). Indeed, the recurrence of such tautomerism was, of course, not to be expected, although in this instance the proof of structure

was supplied by the formation of a well-defined acetyl derivative (XIV). When the dibromo-ester (X) is hydrolysed by means of ethyl alcoholic potash, it behaves like the corresponding dibromo-ester in the dimethyl series and yields the ethoxy-ring acid (XV). The stability of this substance is remarkable, because it is unaltered by strong aqueous alkali even on prolonged boiling and is unaffected by concentrated hydrochloric acid.



The ethoxy-acid (XV) is partly converted into the ring-acid (XXII) with strong hydriodic acid and gives the correct "ethoxy-value" by the Zeisel method. It is, however, with the corresponding methoxy-derivative (XVI) that we have been able to carry out experiments which have enabled us to co-ordinate the formation of these apparently abnormal substances with the other reactions of the series and to show that their formation and properties are in every way consistent with our general hypothesis.

This remarkable substance can be isolated in well-defined *cis*- and *trans*-forms, the *trans*-modification being converted into the *cis*- through the anhydride of the latter. Both isomerides pass on treatment with hydriodic acid into the keto-acid (XVII), which can be characterised by the formation of a well-defined quinoxaline derivative (with *o*-phenylenediamine) and by its conversion, on distillation, into the anhydride of methylethylsuccinic acid (XVIII) (compare Balbiano's acid, T., 1922, **121**, 650). Here then we have

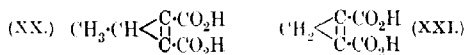


the mechanism of the change revealed, because it will be noticed that the action of hydriodic acid is not a reducing action but merely one by which the group $\text{O}\cdot\text{CH}_3$ is converted into OH in the usual manner.

The hydroxy-acid (XIX) is, however, unstable and passes at once into the open-chain keto-acid (XVII), which is stable to 64 per cent. aqueous potassium hydroxide. These experiments, therefore, afford complete confirmation of our contention that the alteration of the tetrahedral angle which causes the keto-acid and hydroxy-ring acid to be tautomeric in the case of the *gem*-diethyl compound, causes also the hydroxy-ring acid to be the only stable form in the

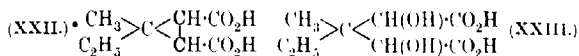
cyclohexane series, and the keto-acid the only stable form in the *gem*-dimethyl series.

The reasons why the alkyloxy-derivatives are formed at all in the instances given are also quite clear, but as these will be dealt with fully in a future paper and are bound up with the chemistry of the *cyclopropene* structures to be mentioned there, it is unnecessary to give them in this communication. It is sufficient here to mention that the isolation of these abnormal alkyloxy-derivatives which was carried out twenty-two years ago and which the later work of Feist on the *cyclopropene* acid (XX) rendered still more difficult to explain, has now proved to be the key to the whole problem of reversible and non-reversible isomerism in this series. Feist's



acid, and still more recently the acid (XXI) (Farmer and Ingold, T., 1921, 119, 2001) did not tend to add on alcohol, because they constituted stable glutaric systems, each containing the necessary mobile hydrogen atom. On the other hand, the acids of the $\beta\beta$ -*gem*-series cannot contain the hydrogen atom and in consequence are incapable of isolation in the unsaturated form, and even when the unsaturated bond is removed by addition, the ring remains unstable unless the tetrahedral angle has been sufficiently deflected. It is scarcely necessary to point out that the addition of alcohol leads to a stable alkyloxy-derivative and the addition of water to either the keto-acid or hydroxy-ring acid, whichever is the more stable, because the presence of the alkyloxy-group does not supply the necessary hydrogen atom for ring rupture.

For the rest, the ring acid (XXII) occurs in well-defined *cis*- and



trans-forms and shows all the usual reactions of acids of this type. As regards stability, they do not undergo fission with mineral acids, and are therefore more stable than the caronic acids, which are completely decomposed under these conditions into terebic acid (compare Perkin and Thorpe, T., 1899, 75, 48). This is, therefore, another indication of stability caused by the alteration of the tetrahedral angle.

Again, the lactonic acid (XIII) is evidently the lactonic acid of the *trans*-dihydroxy-acid, because the corresponding *cis*-dihydroxy-acid (XXIII) is stable and gives a characteristic silver salt.

EXPERIMENTAL.

Methylethylglutaric acid was prepared by the condensation of methyl ethyl ketone with ethyl cyanoacetate in the presence of alcoholic ammonia (Guareschi's general method as modified by Kon, T., 1921, **119**, 818). It was obtained in quite a satisfactory yield.

The anhydride was prepared by boiling the acid with acetic anhydride and distilling the product under diminished pressure. The *anhydride* sets to a crystalline mass on cooling and melts above 25°. It reacts with aniline in benzene solution in the cold to form the *anilic acid*, which was obtained in a crystalline condition (compare T., 1911, **99**, 440), and when recrystallised from a mixture of chloroform and petroleum melted at 105° (Found: C = 67.3; H = 7.5. $C_{14}H_{15}O_3N$ requires C = 67.4; H = 7.6 per cent.).

Dibromination of $\beta\beta$ -Methylethylglutaric Acid.

Dibromination was effected by converting the acid or its anhydride into the acid chloride and then adding bromine. In the case of the acid the following conditions were observed:

Eighty-seven grams of the acid were mixed with 208 grams of phosphorus pentachloride, and the mixture was gently warmed on the water-bath until a clear solution was obtained. To this, 67 c.c. of dry bromine were added in four instalments, and the mixture was heated on the water-bath until free from halogen. After cooling, the product was divided: part being poured into anhydrous formic acid and part into absolute alcohol.

trans-xx'-Dibromo- $\beta\beta$ -methylethylglutaric Acid (XII).—The formic acid solution was gently warmed on the water-bath for two hours and then left in a crystallising dish at the ordinary temperature for slow evaporation. The first crop of the crystals that separated consisted almost exclusively of the *trans*-isomeride. Drained on porous plate, washed with dry benzene, and twice crystallised from a mixture of chloroform and light petroleum (b. p. 100–120°), it melted sharply and decomposed at 173° (Found: Br = 48.2. $C_8H_{12}O_4Br_2$ requires Br = 48.1 per cent.). A further quantity was isolated by treating the residual semi-solid mass, obtained after the formic acid had completely evaporated, with dry benzene. The insoluble granular portion was collected by the aid of the pump and purified in the same way as the first crop.

cis-xx'-Dibromo- $\beta\beta$ -methylethylglutaric Acid.—The *cis*-isomeride was obtained from the benzene-soluble portion and purified by repeated crystallisations alternately from benzene and a mixture of

chloroform and light petroleum. The pure acid melts at 146° (Found : Br = 48.0. $C_8H_{12}O_4Br_2$ requires Br = 48.1 per cent.).

Ethyl $\alpha\alpha'$ -Dibromo- $\beta\beta$ -methylethylglutarate (X).—The crude product of dibromination poured into absolute alcohol was kept over-night. It was then diluted with water and extracted with ether. The ethereal solution was thoroughly washed with dilute sodium carbonate solution and dried. On evaporating, the crude dibromo-ester was obtained as a pale coloured oil, which could not be distilled under diminished pressure without decomposition. From one sample a constant-boiling fraction was obtained ($194\text{--}196^{\circ}/31\text{ mm.}$), and it proved to be the *bromo-lactonic ester* of *methylethylglutaric acid* (XI) (Found : Br = 28.5. $C_{10}H_{15}O_4Br$ requires Br = 28.6 per cent.).

In the subsequent experiments, we therefore used the crude dibromo-ester. Its analysis gave the following result : Found : Br = 37.9. $C_{12}H_{20}O_4Br_2$ requires Br = 41.2 per cent.

Acid Ester.—The sodium carbonate washings of the ethereal solution of the neutral dibromo-ester contained just traces of the acid ester.

If, however, thionyl chloride be substituted for phosphorus pentachloride, a considerable proportion of the acid ester is invariably produced. It does not distil without decomposition. That it is mainly a monobromo-acid ester is proved from the products obtained on hydrolysing it (p. 121).

trans-Lactonic Acid of $\alpha\alpha'$ -Dihydroxy- $\beta\beta$ -methyl-ethylglutaric Acid (XIII).

Twenty grams of the *trans*-dibromo-acid (XII) were dissolved in 200 c.c. of 2*N*-solution of sodium carbonate, and the solution was boiled for two hours. When cold, it was acidified with hydrochloric acid and extracted with ether; the ethereal solution yielding a gum on evaporation, which went completely solid after keeping. Recrystallised from benzene, it melted at 116° (Found : C = 50.9; H = 6.3. $C_8H_{12}O_5$ requires C = 51.0; H = 6.3 per cent.).

It is moderately soluble in all the usual solvents except light petroleum, in which it is practically insoluble.

The *trans*-hydroxy-lactonic acid is a remarkably stable compound. It was recovered unchanged after treatment with boiling 64 per cent. potassium hydroxide solution. Still higher concentrations of alkali, however, brought about deep-seated decomposition, oxalic acid being the only substance that was identified in the products of decomposition.

The *cis*-dibromo-acid yielded the same *trans*-lactonic acid under similar conditions of hydrolysis.

The silver salt is extremely soluble in water and could not be collected in quantity sufficient for analysis.

The acetyl derivative (XIV) was obtained by boiling the acid with a sufficient quantity of acetyl chloride for fifteen minutes. It separated from benzene in small needles, melting at 121°. It is readily soluble in ether, chloroform, or acetone and moderately soluble in benzene (Found: C = 52.1; H = 5.6. $C_{10}H_{14}O_6$ requires C = 52.1; H = 6.0 per cent.).

1-Ethoxy-3-methyl-3-ethylcyclopropane-1:2-dicarboxylic Acid
(XV).

Sixty grams of the dibromo-ester (X) were mixed with an alcoholic potassium hydroxide solution containing 60 grams of the hydroxide, 36 c.c. of water, and 240 c.c. of ethyl alcohol, and boiled under reflux for three hours. The solution was then freed from alcohol, acidified, and extracted with ether. The syrupy residue obtained on evaporation could not be induced to crystallise. However, on treatment with ammonium hydroxide solution ($d\ 0.880$) a crystalline ammonium salt of the ethoxy-acid was isolated, which was further purified by dissolving in alcohol and precipitating by the addition of dry ether. The purified ammonium salt was dissolved in dilute hydrochloric acid and extracted with ether, when the ethereal solution deposited crystals of the ethoxy-acid on evaporation. Recrystallised from benzene, it melted at 150° [Found: C = 55.0; H = 7.5; OEt = 20.3. $C_8H_{11}O_4(OEt)$ requires C = 55.5; H = 7.4; OEt = 20.8 per cent.].

The ethoxy-acid is very stable. It was recovered unchanged (apart from the production of a little tarry matter) after having been boiled for several hours with hydrochloric acid. A treatment with strong alkali solution likewise did not effect any change. However, gentle heating with 80 per cent. sulphuric acid decomposed it into *xx*-methyleneethylsuccinic acid, melting at 103°, with the evolution of carbon monoxide (Found: C = 52.6; H = 7.5. Calc., C = 52.5; H = 7.5 per cent.).

By boiling the ethoxy-acid with hydriodic acid, a gummy mass was obtained, from which a small quantity of *trans*-3-methyl-3-ethylcyclopropane-1:2-dicarboxylic acid (XXII) was isolated.

Action of Strong Methyl Alcoholic Potash on Ethyl xx'-Dibromomethyl-ethylglutarate: Formation of trans- and cis-1-Methoxy-3-methyl-3-ethylcyclopropane-1:2-dicarboxylic Acid and xx'-Dihydroxy-ββ-methyl-ethylglutaric Acid.

To a boiling solution of 202 grams of potassium hydroxide in 600 c.c. of methyl alcohol were added 129 grams of the neutral

di-bromo-ester (X) as rapidly as possible, and the heating was continued for twenty minutes. After evaporating off the alcohol, the residue was dissolved in water, acidified, and extracted with ether, and the ethereal solution dried over calcium chloride.

$\alpha\alpha'$ -Dihydroxy- $\beta\beta$ -methylethylglutaric Acid (XXIII).—The calcium chloride used for drying the ethereal solution was found to have changed partly into a calcium salt of an organic acid. The whole of the calcium chloride mixed with the organic salt was therefore dissolved in dilute hydrochloric acid and extracted with ether. The ethereal solution on slow evaporation deposited beautiful, long needles of *$\alpha\alpha'$ -dihydroxy- $\beta\beta$ -methylethylglutaric acid*. Recrystallised from chloroform, it melted at 80° (Found : C = 46.5; H = 6.6. $C_8H_{14}O_6$ requires C = 46.6; H = 6.7 per cent.).

The *silver* salt was prepared in the usual way. It is a crystalline, white powder (Found : Ag = 51.6. $C_8H_{12}O_6Ag_2$ requires Ag = 51.4 per cent.).

1-Methoxy-3-methyl-3-ethylcyclopropane-1:2-dicarboxylic Acid (XVI).—The dried ethereal solution remaining after separation of the calcium salts was evaporated, and a gum was obtained which completely solidified on keeping. From this, by fractional crystallisation from chloroform, the *cis*- and the *trans*-isomerides of the methoxy-acid were separated. The *trans-acid*, when pure, melts at 149° and crystallises well from a mixture of acetone and light petroleum. It is less soluble in chloroform than its isomeride (Found : C = 53.6; H = 6.7. $C_9H_{14}O_5$ requires C = 53.4; H = 6.9 per cent.).

The *cis-acid* melts at 141° . It is freely soluble in chloroform, acetone and ethyl acetate (Found : C = 53.4; H = 6.7. $C_9H_{14}O_5$ requires C = 53.4; H = 6.9 per cent.).

The Anhydride.—The *cis*-acid, on boiling with acetyl chloride, is readily converted into the anhydride, from which the original acid can be regenerated by boiling it with water. The anhydride is a colourless, mobile liquid boiling at $144^\circ/7$ mm. (Found : C = 58.2; H = 6.0. $C_9H_{12}O_4$ requires C = 58.6; H = 6.5 per cent.).

The *trans*-acid, when heated with acetic anhydride in a sealed tube, is changed into the anhydride of the *cis*-acid, from which the *cis*-acid can be produced by hydration.

α -Keto- $\beta\beta$ -methylethylglutaric Acid (XVII).—This was obtained by hydrolysing the methoxy-acid (XVI) with hydriodic acid. A mixture of 32 grams of the methoxy-acid and 160 c.c. of hydriodic acid (*d* 1.7) was gently heated on the oil-bath. After the temperature had been maintained at 80° for some time, during which period the methyl iodide distilled off, it was raised to the boiling point of the solution, the whole operation taking one and a half hours. When

cold, the solution was treated with just enough sulphurous acid to reduce free iodine and was extracted with ether, the ethereal solution yielding the fluid keto-acid on evaporation. This could not be induced to crystallise. It was, however, characterised by the formation of a well-defined quinoxaline derivative, which was readily formed when the keto-acid was intimately mixed with *o*-phenylenediamine in acetic acid solution and gently warmed. Recrystallised from acetone diluted with water, the *quinoxaline* melted at 216° (Found: C = 64.6; H = 6.2. $C_{14}H_{16}O_3N_2$ requires C = 64.6; H = 6.1 per cent.).

The keto-acid, when distilled under diminished pressure, is converted into the anhydride of methylethylsuccinic acid (XVIII), from which methylethylsuccinic acid was obtained and identified.

Hydrolysis of the Monobromo-acid Ester.

The monobromo-acid ester was obtained as a by-product in the experiment of dibromination of the methylethylglutaric acid, and was hydrolysed with a strong aqueous solution of potassium hydroxide.

trans-3-Methyl-3-ethylcyclopropane-1:2-dicarboxylic Acid (XXII).—A solution containing 60 grams of potassium hydroxide in 50 c.c. of water was heated to boiling. Nineteen grams of the monobromo-acid ester were then cautiously added as rapidly as possible. A vigorous reaction ensued which gradually subsided. When cold, the whole was dissolved in water and acidified with hydrochloric acid, when crystals of the *trans*-acid separated on cooling. The whole of the *trans*-acid was thus separated by filtration. Recrystallised from ethyl acetate, it melted at 221° (Found: C = 55.6; H = 6.8. $C_8H_{12}O_4$ requires C = 55.8; H = 6.9 per cent.).

The *silver* salt is a white powder (Found: Ag = 55.6. $C_8H_{10}O_4Ag_2$ requires Ag = 55.9 per cent.).

The *dianilide* was prepared by heating the acid with excess of aniline at 200° for forty-five minutes. The product separated from dilute alcohol in light scales melting at 291° (Found: C = 75.0; H = 7.1. $C_{20}H_{22}O_2N_2$ requires C = 74.5; H = 6.8 per cent.).

cis-3-Methyl-3-ethylcyclopropane-1:2-dicarboxylic Acid.—The filtrate from the *trans*-acid was extracted with ether, the ethereal solution yielding a semi-solid mass on evaporation. This was spread on a porous tile, drained, and washed with a small quantity of water, which caused the *cis*-acid to become solid. The *cis*-acid was also prepared by heating the *trans*-acid with acetic anhydride in a sealed tube and treating the product with water. It usually melts at 163–165°, but repeated crystallisation from chloroform finally raises its melting point to 180° (with decomposition) (Found: C = 55.5; H = 6.8. $C_8H_{12}O_4$ requires C = 55.8; H = 6.9 per cent.).

The *anhydride* of the *cis*-acid was prepared by heating the acid above its melting point until the evolution of water vapour had ceased. It was characterised by conversion into the *anilic acid*, which was obtained by mixing a benzene solution of the anhydride with a solution of aniline in the same solvent. Crystals separated on agitating the solution with a glass rod. Recrystallised from dilute alcohol, it melted and decomposed at 193° (Found : C = 68·4; H = 6·8. C₁₄H₁₇O₃N requires C = 68·0; H = 6·8 per cent.).

We are indebted to the Chemical Society for a grant which has partly defrayed the cost of the materials used in the investigation.

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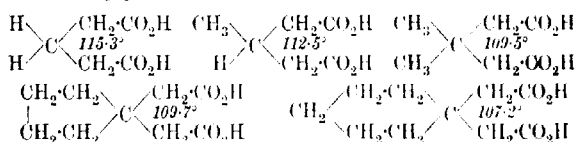
[Received, December 16th, 1922.]

XV.—*The Formation and Stability of spiro-Compounds.*

Part X. spiro-Compounds Derived from cyclo-Heptane.

By JOHN WILLIAM BAKER and CHRISTOPHER KELK INGOLD.

THE main result of the experiments on ring formation which have been carried out in this laboratory during the past eight years has been generally to confirm our view as to the manner in which any factor which changes the normal angle between two valencies of a carbon atom tends as a consequence also to deflect the two remaining valencies. Two types of effect have been examined, (*a*) that which depends on the combined volume of two atoms or groups attached to the carbon atom (T., 1920, **117**, 305, and subsequent papers), and (*b*) that which depends on the inclusion of two valencies in a ring (T., 1915, **107**, 1080, and subsequent papers), and the order and relative magnitude of these two influences may be illustrated by the calculated angles between the two acetic acid residues of the following glutaric acids :



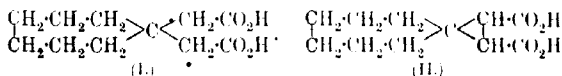
The point has now been reached in the general investigation at which it is necessary more closely to examine individual cases in which real or apparent exceptions to the general hypothesis might possibly be found, and with this object three series of experiments

have been commenced: (a) experiments on the effect of the indirect attachment to a carbon atom of groups of considerable atomic volume, (b) experiments on the dependence of the influence exerted by groups on their electrical character, and (c) experiments on the effect of including two valencies of a carbon atom in rings containing a large number of atoms. The present paper is a contribution to the third of these special investigations.

The hypothesis originally suggested by Beasley, Ingold, and Thorpe, namely, that when two valencies of a carbon atom are included in a ring the remaining two dispose themselves in such a way as to divide up the space external to the ring as equally as possible, leads to the result that an increase in the number of carbon atoms composing the ring is accompanied by a continuous decrease in the inclination between the external pair of valencies. Thus whilst the angles between the valencies binding the acetic acid residues to the ring in *cyclopentane-1:1*-diacetic acid is 109.7° , and in *cyclohexanediacetic acid* is 107.2° , in *cycloheptanediacetic acid* the angle is 105.3° , and in *cyclooctanediacetic acid* it is 103.7° . Hence, on the simple theory, a continuous increase in the ease with which a second ring can be closed by the elimination of groups attached to the acetic acid residues is to be expected as the homologous series is ascended in the manner indicated. It is important to notice, however, that these conclusions are based fundamentally on the supposition that the angles between each pair of valencies composing the various homocyclic rings are actually the internal angles of the corresponding uniplanar regular polygons, namely, 108° , 120° , 128.6° , and 135° , respectively. The normal angle between the carbon-to-carbon valencies of each of the methylene groups of which these rings for the most part consist is 115.3° (Ingold, T., 1920, **117**, 307), and it may reasonably be expected that large divergencies from this value will not be maintained if there is any means whereby they can be lessened. Now in the case of large rings such as *cycloheptane* and *cyclooctane* rings a means does exist whereby the internal angles of the ring can adjust themselves more nearly to the value corresponding with minimal strain: namely, by free rotation around the individual bonds composing the ring of such a kind as to lead to configurations in which the atoms of the ring occupy two or more planes. It is, of course, neither necessary nor desirable to assume that any particular configuration of this kind would in any sense have a permanent character, any more than that the favoured configurations which almost certainly exist in saturated open-chain compounds capable of executing free rotations about single bonds represent permanent configurations of these molecules, especially since at all temperatures

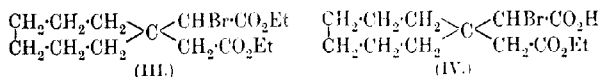
above absolute zero partial or complete relative rotations of the type suggested will presumably be one of the kinds of motion contributing to the internal energy; nevertheless, on general grounds it is only reasonable to suppose that the more the internal angle of the uniplanar ring diverges from the angle of no strain, the more will that ring, by motion compounded of rotations about the individual bonds, tend to pass through multiplanar configurations, and the more, therefore, will the effective mean value of the internal angles of the ring fall below the maximal value which the angle reaches when the ring is uniplanar. Hence, reverting to the original hypothesis of Beasley, Ingold, and Thorpe, it is not to be expected in the case of the *cycloheptane* ring, and still less in the case of the *cyclooctane* ring, that the angle between two valencies external to the ring is actually as small as the simple calculation indicates: indeed it would be unsafe to assume that any continuous decrease in the external angle takes place on passing from *cyclopentane* to *cyclooctane*: *cycloheptane* and *cyclooctane* might occupy anomalous positions resembling *cyclopentane* rather than *cyclohexane* so far as concerns the transmission of strain to attached groups or rings if the conditions are such that multiplanar configurations are predominant. The theoretical problem underlying these considerations is quite insoluble in the absence of more exact knowledge of the forces which give rise to favoured configurations around single bonds and of the manner of distribution of the energy of such motion, and therefore, at the present time, it must be left for experiment to decide, qualitatively at least, whether some internal condition such as that postulated actually does bring about the disappearance of some of the strain which an incautious application of the simple hypothesis would indicate to exist.

The experiments which have been carried out on derivatives of *cycloheptane*-1:1-diacetic acid (I) have shown that in the *cycloheptane* ring there certainly appears to exist some condition which greatly reduces the strain within the ring, and therefore the convergence towards one another of the two acetic acid residues. So much is this the case that the effect of the *cycloheptane* ring in promoting the formation and in enhancing the stability of spirane structures such as the *spirocyclopropane* acid (II) is not only less than it might be expected to be, but is actually somewhat less than that which the *cyclohexane* ring has been shown to exert.

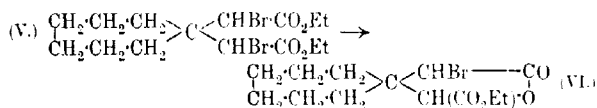


In many respects, however, the experiments which have been

carried out in the *cycloheptane* series have yielded results closely similar to those which Beasley, Ingold, and Thorpe obtained in the *cyclohexane* series. Thus, just as in the *cyclohexane* series it was not found possible to prepare the monobromo-neutral ester (III), although in the *cyclopentane* and *gem*-dimethyl series the corresponding substances can readily be isolated. On the other hand, no difficulty was experienced in isolating a monobromo-acid ester (IV), which was formed in considerable quantity when the Hell-Volhard-Zelinsky bromination product was poured into alcohol. A similar substance was obtained in the *cyclohexane* series, but it was a syrup which could not be purified, and the conclusion that it was of the type of compound (IV) had to be based on its behaviour on hydrolysis. In the present instance, however, the monobromo-acid ester is a well-defined, crystalline solid, so that there can be no question as to its composition, although there is no evidence as to which of the two carboxyl groups is esterified. Again, just

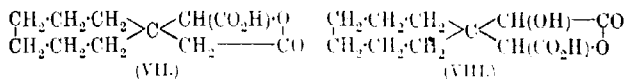


as in the *cyclohexane* series, the dibromo-neutral ester (V) is unstable, since on heating it passes into the bromo-lactone ester (VI) with the elimination of ethyl bromide :



The same remarkable tendency to yield a lactone was not observed in the neutral dibromo-esters of the *gem*-dimethyl- and *cyclopentane* series, and it is a clear indication of the enhanced tendency in the *cyclohexane* and *cycloheptane* series towards the formation of rings by the elimination of groups from the two acetic acid residues.

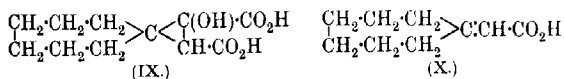
On hydrolysis of the monobromo-acid ester (IV) with concentrated aqueous alkali at 150°, hydrogen bromide was eliminated with the formation of the *spiro*-acid (II), the yield, 38 per cent. of the theoretical, being practically the same as in the *cyclohexane* series. The remainder of the material was converted into the lactonic acid (VII), which is similar in every way to its *cyclohexane* analogue.



Certain remarkable differences between the two series were, however, observed during the investigation of the stability of the *spiro-acid* (II) towards mineral acids. It will be recalled that caronic acid, the analogue of the acid (II) in the *gem*-dimethyl series, readily undergoes ring-fission, forming terebic acid when heated at 200° with 5 per cent. hydrochloric acid, and that the *cyclopentane* analogue is also completely decomposed under the same conditions, although an analogue of terebic acid was not isolated in this case (Becker and Thorpe, T., 1920, 117, 1579). The *cyclohexane spiro-acid*, on the other hand, is an extremely stable substance, which, for example, survives heating with 20 per cent. hydrochloric acid at 240° for six hours (Beasley, Ingold, and Thorpe, *loc. cit.*). Now the stability towards hydrochloric acid of the *cycloheptane spiro-acid* lies between that of the *cyclohexane* acid and of the *cyclopentane* acid, and is definitely less than that of the former; for heating at 200° with 5 per cent. acid has no effect on the *cycloheptane* acid, whilst heating for the same length of time at 240° with 20 per cent. acid completely decomposes it. As in the *cyclopentane* series, it was not found possible to isolate any definite decomposition products, but it was proved in the present case that the observed instability is a property of the spirane structure, and not of the *cycloheptane* ring *per se*; for when *cycloheptane-1:1*-diacetic acid was subjected to similar treatment practically no decomposition took place.

Investigation of the products of hydrolysis of the bromo-lactone ester (VI) gave further evidence that the *cycloheptane spiro*-compounds are neither so readily formed nor so generally stable as the corresponding *cyclohexane* derivatives, and that in these respects the *cycloheptane* series appears to occupy a position between the *cyclohexane* and *cyclopentane* series. In the *cyclohexane* series, the bromo-lactonic ester (type VI) was obtained in *cis*- and *trans*-modifications, which, on hydrolysis with 64 per cent. potassium hydroxide, gave respectively 40 and 27 per cent. yields of the hydroxy-*spiro-acid* (type IX), together with the unsaturated acid (type X) (or its isomeride with the double bond in the ring), and the *cis*- and *trans*-forms of the hydroxy-lactonic acid (type VIII); 15 per cent. aqueous sodium hydroxide gave rise generally to the same products, although in this case the hydroxy-*spiro-acid* was obtained only from the *cis*-bromo-lactone. On the other hand, no hydroxy-*spiro-acid* (type IX) was encountered in the *cyclopentane* series, although a small amount of *cyclopentylideneacetic acid* (type X) and the hydroxy-lactonic acid (type VIII) were recognised amongst the products of hydrolysis. In the *cycloheptane* series, however, the hydrolysis of the bromo-lactone ester (VI), either

with 64 per cent. aqueous potassium hydroxide, or with 15 per cent. sodium hydroxide, yielded the same three products in about the same proportions. In each case, about 90 per cent. of the product consisted of the hydroxy-lactonic acid (VIII); only 3 per cent. of it was accounted for as the hydroxy-*spiro*-acid (IX), and only 7 per cent. as *cycloheptylideneacetic acid* (X).



The small yields of the hydroxy-*spiro*-acid and of the *cycloheptylidene acid* are particularly noteworthy, since they show that neither the tendency to the formation of the *spirocyclopropane* ring, nor the tendency to the elimination of one of the side chains of the substituted *gem*-diacetic acid, is as great in the *cycloheptane* as it is in the *cyclohexane* series.

It should be noted in passing that the side chain eliminated, presumably as glyoxylic acid, in the reaction leading to the *cycloheptylidene acid* was actually identified in the form of oxalic acid, oxidation having occurred at some stage.

A curious point emerged during the attempts to convert the *spiro*-acid (II), which has all the properties usually associated with a *trans*-configuration, into its *cis*-isomeride; for the *cis*-modification appears to be too unstable to be capable of existence, excepting, possibly, in the form of its anhydride. This point is of interest because it indicates that in matters other than those which might be supposed to be directly associated with the deflection of the tetrahedral angle there is actually a gradation of properties on passing from the *cyclopentane*, through the *cyclohexane*, to the *cycloheptane* series. For in the *cyclopentane* series it is only necessary to distil the *trans*-*spiro*-acid under reduced pressure in order to convert it into an anhydride from which the *cis*-acid can readily be obtained; in the *cyclohexane* series, the *trans*-acid must be boiled for some time under atmospheric pressure before distillation; and in the *cycloheptane* series it is necessary to heat the *trans*-acid with acetic anhydride at 240° in order to convert it into an anhydride, which, moreover, on rehydration by means of hot water yields only the original *trans*-acid.

One of the most striking characteristics of the *cycloheptane* derivatives described in the experimental portion of this paper is their remarkable lack of tendency to crystallise. In this respect they resemble, and even excel, their *cyclopentane* analogues. Excepting the *spiro*-acids (II) and (IX), which are crystalline and very similar to the corresponding *cyclohexane* acids, all the products

of hydrolysis described in this paper are liquids, which boil at constant temperatures it is true, but which, even after many months, have refused to show the slightest tendency to solidify. In view of the fact that *cycloheptanediacetic acid* cannot be obtained in large quantities, this absence of tendency to crystallise has proved a serious handicap in the carrying out of the research, but in spite of this we feel that, in the reactions described, the material has been properly accounted for, and that no product of importance has been overlooked; hence it would appear that the experiments form a satisfactory foundation for the provisional conclusions, given on pp. 123, 124, as to the anomalous conditions of strain in the *cycloheptane* ring.

EXPERIMENTAL.

The *cycloheptanone* required for this investigation was prepared from castor oil by the following series of processes: castor oil \rightarrow ricinoleic acid \rightarrow mixture of suberic and azelaic acids \rightarrow calcium suberate \rightarrow *cycloheptanone*. It was then converted into *cycloheptane-1:1-diacetic acid* by the Guareschi method (Day, Kon, and Stevenson, T., 1920, 117, 639). In all, 150 kilos. of castor oil were worked up, giving 130 grams of *cycloheptanediacetic acid*.

A solution of 7 kilos. of commercial sodium hydroxide in 15 litres of water was mixed with 35 litres of alcohol (methylated spirit) in an enamelled iron pan of 100 litres capacity fitted with a steam jacket by means of which the solution was raised to the boiling point while 25 kilos. of castor oil were added with constant stirring. The mixture was kept at the boiling point for one hour, boiled for a further fifteen minutes, diluted to the full capacity of the pan with boiling water, transferred to a mixing tub containing 50 litres of hot water, and then decomposed with 30 litres of dilute sulphuric acid (1:4 by volume). After thorough mixing, the precipitated ricinoleic acid was allowed to rise to the surface, separated from the aqueous liquid, and then washed three times with 80 litres of water. The yield was 21 kilos.

Since ricinoleic acid rapidly polymerises, it is desirable to proceed with the oxidation as soon as possible. The acid was allowed to flow in a slow stream into 40 litres of nitric acid (*d* 1.25), heated to the boiling point in an open, enamelled iron, steam-jacketed pan provided with an efficient draught hood; and vigorously stirred with a stream of compressed air. The reaction, which was started by adding a few c.c. of alcohol, was very vigorous during the first few hours, but further quantities of nitric acid had to be added towards the end of the operation. Finally, the clear aqueous solution was syphoned while still hot from a small residue of oil,

and allowed to crystallise. The crystals, which consisted of a mixture of suberic and azelaic acids, were separated centrifugally. The mother-liquors on concentration yielded a further quantity, the total yield being 5 kilos.

The separation of the mixed acids was carried out as follows. The crude, air-dried product (10 kilos.) was gently boiled with 30 litres of benzene and 3 litres of absolute ethyl alcohol until practically the whole had passed into solution. The liquid was then carefully syphoned from a small insoluble residue, and allowed to crystallise; 2.2 kilos. of nearly pure suberic acid (m. p. 130—136°) separated, and the mother-liquor on concentration gave a further 0.7 kilo. (m. p. 126—132°). The final mother-liquor was evaporated to dryness, and the residue pressed until free from oil and then crystallised from water below 40°. Nearly pure azelaic acid separated, and the mother-liquors, on concentration to small bulk, yielded a crystalline product (1.8 kilos.) the composition of which was almost the same as that of the original mixture of acids. This was added to the next batch.

The suberic acid was dissolved in a small excess of ammonia and the solution evaporated to dryness with a 20 per cent. excess of slaked lime. The residue was dried thoroughly in evacuated steam-ovens.

The distillation of the calcium suberate was carried out in a specially designed cast-iron still, made in two parts, which were flanged and bolted together on an asbestos joint. The diameter of the still was 21 inches, whilst its height was only 4 inches. A wrought-iron delivery tube, which emerged from the centre of the still-cover, was connected by a suitable adapter with a Liebig's condenser. An iron tube, by means of which a stream of nitrogen could be passed through the apparatus, was also let into the still-cover. The still was built into a gas-fired furnace.

The charge of calcium salt (300 grams) was spread in an even layer over the bottom of the still, which was then raised to 450—500° while a rapid stream of nitrogen was passed. The distillate was separated into an aqueous and an oily layer, and the former extracted with ether, the extract being mixed with the oil, and then dried. The crude *cycloheptanone* obtained after distilling the ether was purified by fractional distillation under ordinary pressure, the fraction having b. p. 174—183° being collected for conversion into the diacetic acid.

Bromination of cycloheptanone-1 : 1-diacetic Acid.

The acid (10 grams), mixed with phosphorus pentabromide (44 grams = 4.1 mols.), was heated until hydrogen bromide ceased to be
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evolved, and then treated with the requisite quantity of bromine (8 grams = 1.1 mols. for monobromination, and 16 grams = 2.2 mols. for dibromination), added in small portions at intervals timed to correspond with the speed of absorption. The operation was completed by heating, and was carried out in direct sunlight whenever there was any. The product was poured into three times its volume of ice-cooled alcohol, and the solution, after being heated to the boiling point, poured into cold water. The bromo-esters were extracted with ether, and separated into neutral and acid fractions by means of ether and dilute sodium carbonate in the usual way.

Ethyl Hydrogen α -Bromocycloheptane-1:1-diacetate (IV).—This substance is obtained in 60 per cent. yield on monobromination and in 25 per cent. yield on dibromination. It is obtained in either case by acidifying the sodium carbonate extract and re-extracting with ether. It crystallises in clusters of colourless needles, which, after crystallisation from ligroin, melt at 84–85° (Found: Br = 24.97. $C_{13}H_{21}O_4Br$ requires Br = 24.89 per cent.).

Ethyl α -Bromocycloheptane-1:1-diacetate (III).—The neutral product of monobromination appeared to consist of this substance along with unbrominated cycloheptanediacetic ester, but it was not found possible to separate the two by fractional distillation.

Ethyl $\alpha\alpha'$ -Dibromocycloheptane-1:1-diacetate (V).—The neutral product of dibromination contained approximately the correct amount of bromine for this substance, the constitution of which was established by its conversion into the lactone mentioned below. Since this change takes place on distillation, it was not possible to purify the dibromo-ester by this means.

Lactone of Ethyl Hydrogen α -Bromo- α' -hydroxycycloheptane-1:1-diacetate (VI).—On distillation under reduced pressure, the dibromo-ester rapidly loses ethyl bromide and is converted into the lactone, which distils at 230–234°/20 mm. It is a colourless, exceedingly viscous oil, possessing no tendency to crystallise (Found: Br = 25.32. $C_{13}H_{19}O_4Br$ requires Br = 25.68 per cent.).

Hydrolysis of the Monobromo-acid Ester (IV).

Hydrolysis of the monobromo-acid ester with boiling 6*N* potassium hydroxide gives a mixture of the spirocyclopropane acid (II) and the lactonic acid (VII), but hydrolysis with boiling aqueous sodium carbonate leads to the lactonic acid only.

trans-cycloHeptanespirocyclopropane-2:3-dicarboxylic Acid (II).—A solution of 12 grams of potassium hydroxide in 10 c.c. of water was boiled until the temperature of the liquid reached 150°, when 4 grams of the monobromo-acid ester were added as rapidly as

possible. When the reaction was over, a little water was added to redissolve precipitated salts, and the solution was rendered only faintly alkaline by the addition of hydrochloric acid, filtered, and then strongly acidified with hydrochloric acid at 0°. The crystals were collected and crystallised, either from a large volume of water, or from a mixture of ether and ligroin, from which small needles, m. p. 235°, separated (Found: C = 62.52; H = 7.52; *M*, by titration, = 211.8. $C_{11}H_{16}O_4$ requires C = 62.27; H = 7.55 per cent.; *M* = 212).

The experiments on the stability of this acid towards 5 per cent. hydrochloric acid at 200° and towards 20 per cent. acid at 240° have been described in the introduction. As already stated (p. 127), the *cis*-isomeride could not be isolated.

Lactone of α-Hydroxycycloheptan-1:1-diacetic Acid (VII).—This substance remained in the aqueous mother-liquor from which the *spiro*-acid was precipitated. Isolated by extraction with ether and purified by distillation, it was obtained as an exceedingly viscous gum, which boils at 240–245°/30 mm., but which after many months has refused to crystallise (Found: C = 62.62; H = 7.47. $C_{11}H_{16}O_4$ requires C = 62.27; H = 7.55 per cent.).

The same lactone is the sole product which is obtained when the bromo-acid ester (7 grams) is boiled for six hours with an aqueous solution (175 c.c.) of sodium carbonate (14 grams). It may be isolated by extracting the acidified solution with ether and purified by distillation as before (Found: C = 62.75; H = 7.39 per cent.). The lactone ring is evidently fairly stable, as the substance titrates as a monobasic acid in the cold and gives a *monosilver* salt when silver nitrate is added to a neutral solution of the ammonium salt (Found: Ag = 33.51. $C_{11}H_{15}O_4Ag$ requires Ag = 33.83 per cent.).

α-Hydroxycycloheptan-1:1-diacetic Acid.—This could not be isolated in the free state, but its *silver* salt was obtained by adding silver nitrate to a cautiously neutralised solution of the lactonic acid in excess of warm sodium hydroxide (Found: Ag = 47.38. $C_{11}H_{16}O_5Ag_2$ requires Ag = 48.65 per cent.).

Hydrolysis of the Bromo-lactone Ester (VI).

The hydrolysis of this bromo-lactone with boiling 64 per cent. potassium hydroxide and with boiling 15 per cent. sodium hydroxide yielded the same three products, the hydroxy-lactone (VIII), the unsaturated acid (X), and the hydroxy-*spiro*-acid (IX), in practically the same proportions.

Lactone of αα'-Dihydroxycycloheptan-1:1-diacetic Acid (VIII).—This substance constitutes about 90 per cent. of the product of

hydrolysis by either of the two reagents mentioned. The bromo-lactone (7 grams) was hydrolysed with a boiling solution of 23 grams of potassium hydroxide in 19 c.c. of water just as described on p. 130. The solution, having been rendered only faintly alkaline and filtered, was acidified with hydrochloric acid, and the precipitated oil extracted with ether. The residue obtained on evaporating the ether was triturated with successive small quantities of warm water, which removed the hydroxy-*spiro*-acid, and the sparingly soluble residue was fractionally distilled under diminished pressure. After the cycloheptylidene acid had passed over, the hydroxy-lactone was obtained as an exceedingly viscous liquid, b. p. 263–267°/30 mm., which has hitherto resisted all attempts to make it crystallise. It has a powerful, characteristic odour reminiscent of decaying cocoa-nuts (Found: C = 58.43; H = 7.24. $C_{11}H_{16}O_5$ requires C = 57.88; H = 7.07 per cent.).

The lactone ring is evidently fairly stable, because the substance titrates as a monobasic acid in the cold (Found: $M = 227.4$. Calc., 228), and gives a *monosilver* salt when silver nitrate is added to a neutral solution of its ammonium salt (Found: Ag = 31.0. $C_{11}H_{16}O_5Ag$ requires Ag = 2.2 per cent.).

αα'-Dihydroxycycloheptane-1:1-diacetic Acid.—This acid did not appear to be capable of existence in the free state, but its *disilver* salt was obtained by adding silver nitrate to a neutralised solution of the lactonic acid in excess of sodium hydroxide (Found: Ag = 46.84. $C_{11}H_{16}O_6Ag_2$ requires Ag = 46.94 per cent.).

cycloHeptylideneacetic Acid (X).—As mentioned above, this substance is obtained as a "low" fraction in the distillation of the hydroxy-lactone. In the crude state, it boils at 155–160°/20 mm., and, on redistillation, at 158°/20 mm. (compare Wallach, *An. den.*, 1900, 314, 157). It is a colourless, fairly mobile liquid, having a characteristic odour. It instantly decolorises cold, alkaline permanganate and absorbs bromine (Found: C = 69.53; H = 8.84. Calc., C = 70.08; H = 9.15 per cent.). It yields an insoluble *silver* salt (Found: Ag = 40.66. $C_9H_{13}O_2Ag$ requires Ag = 41.35 per cent.), by means of which the acid itself can conveniently be purified. The yield of the acid is 7 per cent. of the theoretical.

αβ-Dibromocycloheptaneacetic Acid (?).—Wallach (*loc. cit.*) mentions that cycloheptylideneacetic acid forms a solid dibromo-additive product, but he neither describes it nor even records its melting point. We therefore employed the very small quantity of material at our disposal in the endeavour to characterise the unsaturated acid more completely by means of its dibromo-additive product. A solution of the unsaturated acid (0.33 gram) in 1 c.c. of chloroform was gradually treated with 4.3 c.c. of a chloroform

solution containing the correct quantity of bromine. On slow evaporation of the chloroform, crystals separated, which were drained on porous porcelain and crystallised from a very small quantity of chloroform. Colourless crystals, m. p. 124—125°, were obtained (Found: Br = 53.16. $C_9H_{11}O_2Br_2$ requires Br = 50.93 per cent.).

cycloHeptanespirocyclopropan-2-ol-2 : 3-dicarboxylic Acid (IX).—This acid constitutes 3 per cent. of the product obtained by hydrolysis of the bromo-lactone ester, and is contained in the aqueous extract produced by triturating with water (p. 132). On slow evaporation, the aqueous solution deposits the acid in colourless, cubical crystals, which after crystallisation from a mixture of ether and ligroin melt at 195° (Found: C = 57.85; H = 6.8; *M*, by titration, = 112.3. $C_{11}H_{16}O_5$ requires C = 57.88; H = 7.06 per cent.; *M* = 112).

The acid gives no colour with ferric chloride, and does not decolorise alkaline permanganate or bromine dissolved in acetic acid.

Recognition of Oxalic Acid.—The aqueous solution from which all other products of hydrolysis of the bromo-lactone ester had been extracted with ether (p. 132) was evaporated to dryness with the occasional addition of a little hydrochloric acid. The solid residue was ground and extracted with boiling acetone, which on evaporation gave a dark residue. This was dissolved in boiling water, and the solution decolorised by means of animal charcoal and allowed to evaporate at 50°. Colourless crystals of oxalic acid separated, which were identified in the usual way.

We desire to record our thanks to the Royal Society for a grant which has defrayed part of the heavy expense incurred in this investigation.

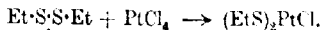
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[Received, December 15th, 1922.]

XVI.—*Varying Valency of Platinum with Respect to Mercaptanic Radicles.*

By SIR PRAFULLA CHANDRA RAY.

THE chloromercaptide $(EtS)_2PtCl$, containing tervalent platinum, obtained by the interaction of platonic chloride and ethyl mercaptan (T., 1919, 115, 872), is also produced from diethyl disulphide under similar conditions; during the reaction chlorine is evolved:



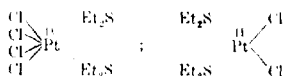
An alternative explanation is that, on account of its greater affinity for sulphur, the platinum not only parts with three of its chlorine atoms but has its additional latent valencies revived, the chloromercaptide being in reality a derivative of quinquevalent platinum and a sulphonium compound, $\begin{matrix} \text{Et}\cdot\text{S} \\ \text{Et}\cdot\text{S} \end{matrix} \gg \text{PtCl}$.

The quinque- and the sexa-valency of platinum are established by the compounds, $(\text{C}_2\text{H}_5)_3\text{S}_2\cdot\text{PtCl}_3$ and $(\text{C}_2\text{H}_5)_3\text{S}_3\cdot\text{PtCl}_4$, already described (T., 1922, 121, 1283); these are examples of the sulphonium derivatives which the author has been investigating during the last seven years. Diethyl sulphide also yields with platinic chloride two chloromercaptides having the empirical formulae $(\text{Et}_2\text{S})_2\text{PtCl}_4$ and $(\text{Et}_2\text{S})_2\text{PtCl}_2$.* The former has been obtained in well-defined crystals and has been proved in acetone solution to be a non-electrolyte. Cryoscopic molecular weight determination in benzene solution also confirms the same conclusion.

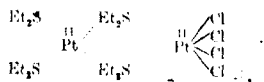
I : 4-Thiazan, $\text{S} < \begin{matrix} \text{C}_2\text{H}_4 \\ \text{C}_2\text{H}_4 \end{matrix} > \text{NH}$, yields with hydrogen chloride the expected hydrochloride, $\text{C}_4\text{H}_9\text{NS}\cdot\text{HCl}$. Davies finds that the compound with platinic chloride has the formula, $\text{B}\cdot\text{HCl}\cdot\text{PtCl}_4$ (T., 1920, 117, 298) and he erroneously regards it as the chloro-platinate of the base: had it been so, it should have conformed to the formula $(\text{B}\cdot\text{HCl})_2\cdot\text{PtCl}_4$. The compound in question is possibly a chloromercaptide, having the formula $\text{Cl}_4\text{Pt}\cdot\text{S} < \begin{matrix} \text{C}_2\text{H}_4 \\ \text{C}_2\text{H}_4 \end{matrix} > \text{NH}\cdot\text{HCl}$, in which platinum is sexavalent.

Direct evidence of the variation in the valency of platinum has been obtained by the interaction of platinic chloride and the following mercaptans or rather their potassium salts, which have been found to be more reactive:—(1) 2-thiol-5-thio-4-phenyl-4 : 5-dihydro-1 : 3 : 4-thiodiazole, $\begin{matrix} \text{NPh}\cdot\text{N} \\ \text{CS} \cdots \text{S} \end{matrix} < \text{SH}$, and (2) dithio-ethylene glycol, $\text{C}_2\text{H}_4(\text{SH})_2$.

* These can be represented on the basis of Werner's co-ordination theory:



or, according to Tschugaeff and Subbotin (*Ber.*, 1910, 43, 1200),



Tervalent Platinum.

The product of interaction in each case has been found to be a well-defined compound, which admits of reproduction under the conditions of formation; these have been studied with great care. It has already been shown that if to a concentrated aqueous solution of the potassium salt of the above thiodiazole a dilute solution of chloroplatinic acid is added in a thin stream, a product is obtained which consists of a mixture of equal proportions of compounds of tervalent and bivalent platinum (T., 1919, **115**, 875); by suitably adjusting the concentrations of the participants, the compound of tervalent platinum has now been isolated in a state of purity. By slightly modifying the process, the corresponding chloromercaptide has also been obtained.

Ter-, Quadri-, Quinque-, Sex-, and Octa-valent Platinum.

The mercaptan most suitable to the preparation of this series is dithioethylene glycol; although it is a dithiol, only one atom of hydrogen of the thiol groups is replaceable by potassium. The substitution of an atom of potassium seems to exercise a sort of inhibitory influence on the second hydrogen atom of the thiol group—in fact, the latter becomes so inert as not to be assailable by the chlorine atoms of platonic chloride. Even chloropierin, which is a very reactive agent, yields with the mercaptide only the compound $[(\text{SH}\cdot\text{C}_2\text{H}_4\cdot\text{S})_3\text{C}_2\text{H}_4\text{O}]$ (T., 1919, **115**, 1308).

In the present instance, the reaction takes place as follows:— $x\text{SH}\cdot\text{C}_2\text{H}_4\cdot\text{SK} + \text{PtCl}_4 \rightarrow \text{Pt}(\text{S}\cdot\text{C}_2\text{H}_4\cdot\text{SH})_x$, where $x = 3, 4, 5, 6$, or 8. By using solutions of the reagents of definite strengths and regulating the temperature of the reaction, compounds have been obtained in which platinum functions as ter-, quadri-, quinque-, sex-, and octa-valent, respectively. For instance, at the temperature of the laboratory (25–30°) sexavalent platinum compounds have generally been obtained; but by suitably varying the concentrations of the parent solutions, quinquevalent compounds have been secured at this temperature. If, however, instead of changing the strength of the above solutions, the temperature of the solution of the potassium salt be reduced to 5–15° (the platonic chloride solution being kept between 25–30°), only octavalent compounds will be produced; similarly, by regulating the range of temperature between 60° and 65°, quinquevalent compounds are formed; at about 80°, quadrivalent ones are obtained, whereas at about 100° the product is uniformly tervalent. At intermediate temperatures mixtures are formed. These reactions have been repeated in almost all cases two to three dozen times under the

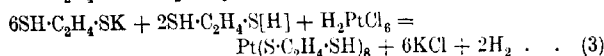
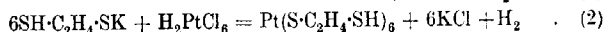
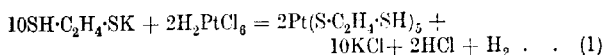
above conditions, with identical results. In fact, it has been well established that the particular valency which platinum will assume is a function of either of the two variables, concentration and temperature.

This result might well have been expected from a consideration of the kinetic theory of molecules. As increase of temperature has the effect of increasing the mobility of the molecules, the platinum atom is not placed in a favourable position to attract its full quantum of mercaptanic radicles. Conversely, if the temperature of the solution is lowered, the molecular velocity will diminish and consequently the platinum atom will be in a position to develop its maximal group valency. It is also a well-known fact that increase of temperature tends to dissociate complex or heavier molecules into simpler ones, and the particular instance here in the case of compounds of platinum, the complexity of which diminishes with increasing temperature, falls within the scope of this general observation. In other words, the higher the temperature of reaction the lower the valency of platinum.

The place of platinum in the periodic table would naturally lead us to expect that, like iridium, it should behave as trivalent and, like osmium, as quadri-, sexa-, and octa-valent. Ruff and Tschirch have shown that the formation of the fluorides, OsF_4 , OsF_6 , OsF_8 , depends on the temperature, the rate of flow of the fluorine current, and the particular physical condition of the osmium (*Ber.*, 1913, 46, 929), and this fact is fairly well borne out in the case of the platinum derivatives which form the subject of the present communication.

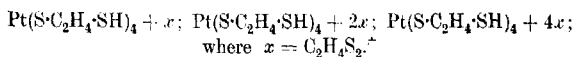
It is not easy to give equations of the reactions involved in the formation of the above compounds and to account for the variation in the valency of platinum. The interaction of diethyl disulphide, (Et_2S_2) and chloroplatinic acid results in the formation of the compound $(\text{EtS})_2\text{PtCl}$ with evolution of chlorine. As diethyl disulphide itself results from the oxidation of ethyl mercaptan, the liberated chlorine cannot further act on the former and hence the presence of any impurity in the shape of oxidation product in this chloromercaptide is precluded. Platinum is evidently trivalent in this compound. When, again, chloroplatinic acid acts on potassium thiazole, the platinum parts with all the chlorine atoms, but contrary to expectation a derivative is obtained in which the metal functions as trivalent. Of course by doubling the formula the metal may be represented as quadrivalent; when, however, it is borne in mind that the chlorides of iron and iridium, the analogues of platinum in the transitional group, have the simpler formulae FeCl_2 and IrCl_2 , respectively, it is scarcely likely

that the platinum mercaptide should have a more complex formula. Similar arguments would support the formula $(\text{SH}\cdot\text{C}_2\text{H}_4\cdot\text{S})_3\text{Pt}$ for the dithioethylene glycol derivative. The formation of quadrivalent platinum mercaptide may naturally be expected; it is not easy to account for the existence of quinque-, sexa-, and octa-valent mercaptides. From considerations of the physical properties of chloroplatinic acid, for example, ionisation, absorption spectrum, and heat of neutralisation, the formula H_2PtCl_6 is assigned to it. As a working hypothesis, the formation of the above compounds may be explained according to the following equations, although objection may be raised that no direct proof of the evolution of hydrogen is available :



In the last reaction, the two molecules of free mercaptan are produced by the hydrolysis of two molecules of potassium mercaptide, the motive of the reaction being the affinity of the sulphur atom of the univalent radicle $\text{SH}\cdot\text{C}_2\text{H}_4\cdot\text{S}\cdot$ for platinum, and hence in the formation of the octavalent compound the hydrogen atom shown in brackets is displaced so as to enable the sulphur atom to enter into direct relationship with the metal, and satisfy its maximum valency. It is well known that certain radicles, simple or compound, enable certain elements to develop their maximum latent valencies. Thus sulphur, which in regard to chlorine is either bi- or quadri-valent, behaves as sexavalent when combining with fluorine or iodine; platinum in respect to the radicle $\text{SH}\cdot\text{C}_2\text{H}_4\cdot\text{S}\cdot$ thus has varying valencies depending on the temperature and concentration of the latter.

On the other hand, it might be urged that chloroplatinic acid would act as if it had the formula $\text{PtCl}_3\cdot 2\text{HCl}$; there is then the possibility of chlorine being liberated, in some instances at any rate, which would oxidise a portion of the dithioethylene glycol to $(\text{C}_2\text{H}_4\text{S}_2)_x$; the latter, being insoluble in ordinary solvents, might be expected to contaminate some of the products. The presence of this oxidation product is, however, highly improbable. Let it be supposed that the reaction is only quantitative in the case of quadrivalent platinum and that the other products are merely mixtures. These, according to the results of the actual experiments, should be represented as



In other words, the amount of the impurity occurs in exact multiple proportions of the molecule $\text{C}_2\text{H}_4\text{S}_2$. In mixtures, however, one would expect the impurity to occur in indefinite proportions.

Another equally untenable position to which the above supposition would lead is that the lower the temperature of the reaction the larger the amount of the oxidation product, the maximum oxidation taking place at 5–15° and the minimum at 100°, that is, at the temperature yielding the tervalent platinum compound. The presence of any accidental foreign substance thus seems to be out of question. Indeed the octadic character of platinum, far from being an anomaly, is to be welcomed as justifying its place in group viii of the periodic system.

EXPERIMENTAL.

Tervalent Platinum.

Thiodiazole and Platinic Chloride.—To 0.5652 gram of the potassium salt, dissolved in 10 c.c. of water, were added with stirring 2 c.c. of chloroplatinic acid (1 c.c. = 0.0301 Pt). The flocculent, orange precipitate obtained was washed with water, dried in a vacuum desiccator, powdered, and treated successively with hot alcohol and benzene (L., 1919, **115**, 876) to extract the impurities (Found: Pt = 22.62; S = 31.88. $\text{C}_{24}\text{H}_{15}\text{N}_6\text{S}_9\text{Pt}$ requires Pt = 22.59; S = 33.03 per cent.). If, however, dilute solutions of the reactants be used, a chloromercaptide will be formed (see under quinquevalent platinum).

Dithioethylene Glycol and Platinic Chloride.—The *modus operandi* is the same as described under sexavalent platinum, the temperature of the mercaptide solution being, in this case, about 100° (Found: Pt = 41.05; S = 39.66; C = 15.24; H = 3.31. $\text{C}_6\text{H}_{12}\text{S}_6\text{Pt}$ requires Pt = 41.13; S = 40.51; C = 15.13; H = 3.15 per cent.).

Quadrivalent Platinum.

Dithioethylene Glycol and Platinic Chloride. The quadrivalent compound of platinum produced by the interaction of dithioethylene glycol and platinic chloride has already been described (*loc. cit.*, p. 87E); but in the present instance the potassium derivative of the mercaptan was employed. By using it in the same concentration as in the cases of ter-, quinque-, sexa-, and octa-valent derivatives, but increasing the temperature to 80°, the desired

* Analysis cannot discriminate between $\text{SH}\cdot\text{C}_2\text{H}_4\cdot\text{S}$ and $\text{C}_2\text{H}_4\text{S}_2$, the difference being only one atom of hydrogen.

compound was obtained (Found: Pt = 34.34; S = 45.68; C = 16.57; H = 3.33. $C_8H_{20}S_8Pt$ requires Pt = 34.39; S = 45.14; C = 16.93; H = 3.54 per cent.).

Triethylene Trisulphide and Platinic Chloride.—The product of interaction is a crystalline compound conforming to the formula $(C_2H_4)_3S_3PtCl_4$, in which platinum behaves either as tetrad or hexad (see above).

Quinquevalent Platinum.

Diethyl Disulphide and Platinic Chloride.—When an alcoholic solution of the components is heated under reflux on the water-bath for three to four hours, the solution gradually becomes turbid, an orange precipitate forms, and chlorine is continuously evolved. The compound has the empirical formula $(C_2H_5S)_2PtCl$, but in reality it is a pentad derivative of the metal. The same compound is also formed in the cold when a concentrated alcoholic solution of the parent substances is set aside for twenty-four hours or more [Found: Pt = 54.51; Cl = 9.95; S = 18.11. $Pt(C_2H_5S)_2Cl$ requires Pt = 55.02; Cl = 10.09; S = 18.19 per cent.].

It is, in fact, the same compound which has already been described as formed by the interaction of ethyl mercaptan and chloroplatinic acid. If instead of this simple mercaptan one with a complex radicle, for example, thiodiazole, be used, a corresponding chloromercaptide will be obtained.

Thiodiazole and Platinic Chloride.—To 4 c.c. of diluted chloroplatinic acid (= 0.0400 gram Pt) were added drop by drop with constant stirring 7.5 c.c. of a dilute solution of the potassium salt (= 0.1058 gram). The precipitate was washed with water, dried in a vacuum, and treated successively with alcohol and benzene (Found: Pt = 28.19; Cl = 4.86. $C_{16}H_{10}N_4ClS_6Pt$ requires Pt = 28.86; Cl = 5.00 per cent.).

Triethylene Trisulphide and Platinic Chloride.—The trisulphide has also been shown to yield another compound with platinic chloride which has the formula $(C_2H_4)_3S_2PtCl_3$, one atom of sulphur being detached from the trisulphide during reaction. The platinum here may be regarded as ter- or quinque-valent.

Dithioethylene Glycol and Platinic Chloride.—To 0.4330 gram of the potassium salt, dissolved in 8.4 c.c. of water at the ordinary temperature (25–30°), were added with vigorous shaking 23 c.c. of platinic chloride solution (1 c.c. = 0.0067 gram Pt). The light brown precipitate was treated as described under sexavalent platinum. The same compound was obtained when the experiment was conducted under the same conditions as given below under sexavalent platinum, the only variation being that the temperature

was kept between 60—65° (Found: Pt = 29.78; S = 48.01; C = 18.46; H = 4.54. $C_{10}H_{25}S_{10}Pt$ requires Pt = 29.54; S = 48.50; C = 18.13; H = 3.78 per cent.).

Sesavalent Platinum.

As the mercaptide, $C_2H_4(SH)(SK)_2$ * is the parent substance from which most of the derivatives of platinum have been obtained, and as it has not been described before, its preparation is given here in detail. A large excess of concentrated alcoholic potash is added to dithioethylene glycol. The mixture, which solidifies when stirred, is rapidly filtered with suction, and the solid washed with alcohol. Care should be taken to limit the quantity of alcohol used, for the potassium salt is appreciably soluble in that menstruum. The solution remains clear only for about half an hour and then begins to turn turbid owing to aerial oxidation and the formation of the disulphide, $C_2H_4S_2$.

Dithioethylene Glycol and Platinic Chloride.—The hexad derivative is the one which was almost invariably formed when about 12 c.c. of platinic chloride solution (1 c.c. = 0.0260 gram Pt) were added to 0.5500 gram of the potassium salt of dithioethylene glycol, dissolved in 15 c.c. of water at temperatures between 25—30°. The platinum chloride solution was introduced in a thin stream into the vigorously agitated liquid and the operation was finished in less than five minutes. The granular, light-brown precipitate was vigorously shaken, and a large volume of water added to the mixture to preclude the possibility of the formation of potassium chloroplatinate. It was washed first with water, then with alcohol, and finally with ether, and dried in a vacuum over sulphuric acid (Found: Pt = 26.00; S = 51.40; C = 18.94; H = 3.40. $C_{12}H_{20}S_{12}Pt$ requires Pt = 26.09; S = 50.85; C = 19.07; H = 3.97 per cent.).

Diethyl Sulphide and Platinic Chloride.—A concentrated alcoholic solution of the above two components was set aside for two to three days. The crystalline products which were obtained were dissolved in boiling alcohol. The crop which was deposited on cooling conformed to the formula $(Et_2S)_2PtCl_4$ and had the m. p. 198°. On concentration of the mother-liquor, the product of the formula $(Et_2S)_2PtCl_2$, m. p. 77°, was obtained † (Found: Pt = 44.01; Cl = 16.05. Calc. for $C_8H_{20}Cl_2S_2Pt$, Pt = 43.97; Cl = 15.85 per cent.).

* Analysis of the potassium salt. Found: K = 29.99. $C_2H_4S_2K$ requires K = 29.55 per cent.

† Both these compounds have already been described, but the method of formation was quite different (*Jahresber.*, 1888, 1, 1419; Tschugueff, *loc. cit.*).

Octavalent Platinum.

Dithioethylene Glycol and Platinic Chloride.—The conditions of the experiment were almost the same as described under sexavalent platinum, the only difference being that the temperature was kept at 5–15° (Found : Pt = 21.00; S = 54.79; C = 19.97; H = 3.89. $C_{16}H_{40}S_{16}Pt$ requires Pt = 20.94; S = 54.41; C = 20.36; H = 4.25 per cent.).

The absence of chlorine was proved in all these compounds.

Diethyl Sulphide and Platinic Chloride.—The preparation of the compound $(Et_2S)_2PtCl_4$ has been described under sexavalent platinum [Found : Pt = 37.64; Cl = 27.20; *M*, by the cryoscopic method (in benzene), = 540. $C_8H_{20}Cl_4S_2Pt$ requires Pt = 37.96; Cl = 27.36 per cent.; *M* = 519.]

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[Received, April 3rd, 1922.]

XVII.—*Phenyltrimethylammonium Perhaloids.*

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It has been known for a long time that both organic and inorganic haloids combine with one or more molecules of free halogen to give crystalline substances termed perhaloids, of which KI_3 , NMe_4I_3 , NMe_4ICl_2 are typical examples. Comparatively little, however, seems to be known about the chemical structure or the reactions of these substances. The purpose of many investigations in the past would seem to have been directed principally towards establishing whether there exists an upper limit to the combining power of the atoms forming such complexes, in order to test the validity of this or that hypothesis concerning residual valence, partial valence, or the contra-valence of the atoms concerned.

This communication describes experiments carried out with phenyltrimethylammonium haloids in order to establish the following points :

- (a) To which atom in a quaternary ammonium salt the capacity for the addition of free halogen is due.
- (b) To what extent and under what conditions interconversion of periodides, perbromides, chloro-iodides, and bromo-iodides is possible.
- (c) Whether isomeric perhaloids can be prepared containing the same atoms differently arranged, or

(d) Whether from a given set of halogen atoms one favoured arrangement of such atoms always exists.

(e) Whether any trustworthy means of degradation of a perhaloid could be devised in order that the structural arrangement of its atoms could be deduced.*

In an investigation of perbromides derived from aromatic nitrogenous bases, de Vries (*Annalen*, 1905, **343**, 128) concluded that, since nitrogen-free compounds such as the haloid salts of oximes and oxonium bases also give perhaloids, which he considered analogous to the perhaloids of quaternary ammonium salts and of the hydrobromides of primary, secondary, and tertiary amines, the affinity which unites the added halogen atoms to the molecule is *not* dependent on the nitrogen atom but on the halogen atom which is united to the nitrogen. As the validity of this reasoning depends on the similarity in chemical properties between the perhaloids of oxonium bases and those of quaternary ammonium salts, the authors felt that this assumption of de Vries should be placed on firmer ground. Non-halogen salts of a quaternary ammonium base, that is, phenyltrimethylammonium nitrate and sulphate, were treated with chlorine, bromine, and iodine, but in no case have nitrates or sulphates with added halogen been obtained. Very small quantities of QmBr_3 , \dagger QmI_3 , QmI_5 , together with much unchanged nitrate or sulphate, were obtained in each case. These experiments confirmed the view that the necessary condition for obtaining perhaloids is that a halogen atom shall be present as a salt-forming element in the original quaternary ammonium salt, that the affinity which holds the added halogens emanates from the *N*-halogen atom, but not in an indeterminate way from the molecule as a whole nor from the nitrogen atom.

It is interesting to notice that, at one time, Masson and Kirkland (*T.*, 1889, **55**, 132) believed that they had evidence of the

* In connexion with the perhaloids the following terms are employed in this communication :

1. *N*-Halogen, by which is meant the halogen atom in a perhaloid which is united directly to the nitrogen atom of the base.

2. Added-halogens, which are those halogen atoms in a perhaloid (intimately associated with the *N*-halogen) which are most easily detached from the molecule. This term does *not* refer to the method of formation; for example, by treatment of quaternary ammonium iodides with chlorine, derivatives of the quaternary ammonium chloride are obtained: $\text{R}_4\text{NI} + \text{Cl}_2 \rightarrow \text{R}_4\text{NCl}_2\text{I}$. In the perhaloid so obtained, the added halogens are considered to be ICl —not chlorine—and in the same way chlorine and not iodine would be considered the *N*-halogen.

3. Parent quaternary salt, which is the salt resulting from a perhaloid by the elimination of the added halogens.

\dagger $\text{Qm} = \text{NPhMe}_3$.

formation of perhaloids of phosphonium compounds derived from tetraethylphosphonium sulphate, for example, $(\text{PEt}_4)_2\text{SO}_4\text{Br}_{22}$ and $(\text{PEt}_4)_2\text{SO}_4\text{Br}_{12}$. These authors, however, found that after crystallisation from alcohol these compounds were free from sulphate.

De Vries regarded perhaloids as molecular compounds which, being unstable, easily break down into relatively stable, simpler compounds, but the term seems misleading as applied to quaternary ammonium perhaloids, for most of these possess considerable stability, definite crystalline form, definite melting point, and can be recrystallised from such a solvent as glacial acetic acid. Emphasis is laid on this point because the so-called instability of quaternary ammonium perhaloids has been much exaggerated in the past. It will be shown later that such perhaloids in the finely powdered, solid state have dissociation pressures at temperatures below 94° which, in most cases, are actually lower than those of the parent quaternary ammonium salts.

To obtain information on points (b), (c), (d), and (e), the quaternary ammonium chloride, bromide, or iodide in glacial acetic acid solution was treated with halogen. The perhaloid thus obtained could then be treated further with halogen, but it soon became evident that the same compounds were being obtained by different methods of preparation and that the constitutions of the compounds could not be deduced from their methods of formation, but would have to be elucidated by the nature of the degradation products.

The first method of degradation consisted in the use of ethyl malonate, which was found to be a very gentle and convenient method of removing halogens. An example of its use is furnished by the degradation of $\text{NPhMe}_3\text{Cl}_3\text{ICl}_3$, which on treatment with ethyl malonate yields $\text{NPhMe}_3\text{Cl}_3\text{ICl}$.

As a more vigorous means of withdrawing halogens, acetone (dry) at temperatures from 18° to its boiling point was found to be particularly useful.* On treatment with acetone, these perhaloids (except those containing the group I_2 or I_4) lose their added halogens and the parent quaternary ammonium salt is precipitated, for example, QmCl_3ICl with acetone gave QmCl ; $\text{QmCl}_3\text{ICl}_3$ gave QmCl ; QmBr_3IBr gave QmBr ; QmBr_3Br_2 gave QmBr ; QmBr_3Cl_2 gave QmBr ; and QmBr_3ICl gave QmBr . Periodides of the types QmI_2I_2 and QmI_4 , as also bromodi-iodides, QmBr_2I_2 , are not,

* Comparative experiments were carried out at temperatures from 18° to the boiling point of acetone and during periods of time varying from fifteen minutes to sixty hours. In every case identical products were obtained in the same reaction. As is to be expected, the velocity of the reaction is affected by the temperature. On account of their different velocities the reactions with the individual perhaloids were carried out at different temperatures in order that they might be completed within a single day.

however, attacked appreciably by acetone under these conditions. From the fact that the acetone treatment of different perhaloids may give rise to the elimination of chlorine alone, bromine alone, iodine and chlorine, or iodine and bromine the likelihood that acetone may exercise too marked a preferential affinity for one halogen rather than another is small. This acetone treatment, first employed by de Vries and by Hantzsch for the degradation of perbromides and extended by the authors to mixed perhaloids in general, is probably the most trustworthy method for ascertaining the constitution of the parent quaternary ammonium salt. It has the great advantage over all methods using water or other hydroxylic solvents that secondary changes are eliminated.

After degradation had indicated the nature of the parent quaternary salt and of the added halogens, a synthesis from these was attempted either in acetic, hydrobromic, or hydrochloric acid solution, and in every case the identity between the synthetic product and the original perhaloid was complete.

In Table I are summarised the methods of formation of the different perhaloids, their degradation products, products of chlorination, etc.

It is to be noticed that the capacity for the direct addition of halogens by the quaternary ammonium salts (without interchange of reacting elements) is greatest in the case of the quaternary ammonium bromide. This is shown in Table II. Whereas the iodide gives rise to only one type of perhaloid, that is, the periodides, and the chloride only to the chloro-iodochlorides, it is seen that the bromide gives rise to five distinct types, of which QmBr_2Cl_2 is the least stable. The most interesting of these types is QmBr_2ICl , which contains three atoms of different halogens united together. Its constitution follows from its degradation by the acetone treatment into the quaternary ammonium bromide. Many attempts were made to prepare the isomeric substance QmCl_2IBr , but without success. When the chloride was treated with iodine monobromide, QmCl_2ICl and QmBr_2IBr resulted. It appears as if the arrangement QmCl_2IBr is essentially unstable.

Replacement of Halogen Atoms in Perhaloids.

From a study of Table I it is seen that by the action of a halogen on a perhaloid or on a quaternary ammonium salt, an exchange of the *N*-halogen or of the added halogen frequently takes place. The following generalisations have been observed with regard to these replacements :

1. Chlorine invariably replaces the *N*-halogen in the quaternary ammonium iodide or in periodides. It also replaces the *N*-bromine

TABLE I.

Method of formation.	Formula.	Product of acetone treatment.	Product of chlorination, unchanged	Product of bromination, QmBr_2Br_2 (traces)	Product of iodination, QmI_2 (10%)	Product from IBr or ICl .
$\text{QmCl}_2\text{ICl} + \text{acetone}$	QmCl	—	—	—	—	—
$\text{QmBr}_2\text{Br}_2 + \text{acetone}$	QmBr	—	QmBr_2Cl_2	QmBr_2Br_2	QmBr_2I_2	QmCl_2ICl QmBr_2IBr
$\text{NPhMe}_2 + \text{MeI}$	QmI	—	$\text{QmCl}_2\text{ICl}_2 + \text{QmCl}_2\text{ICl}$	QmBr_2IBr	$\text{QmI}_2, \text{QmI}_2\text{I}_2$, etc.	QmBr_2ICl QmBr_2IBr QmI_2I_2
$\text{QmI} + \text{excess Cl}_2$	$\text{QmCl}_2\text{ICl}_2$	QmCl	unchanged	unchanged	—	—
$\text{QmBr}_2\text{IBr} + \text{excess Cl}_2$	QmCl_2ICl	"	$\text{QmCl}_2\text{ICl}_2 + \text{QmCl}_2\text{ICl}$	"	unchanged	—
$\text{QmCl} + \text{ICl}$	QmBr_2ICl	QmBr	$\text{QmCl}_2\text{ICl}_2$	"	"	—
$\text{QmBr} + \text{IBr}$	QmBr_2IBr	"	"	"	"	—
$\text{QmBr} + \text{Cl}_2$	QmBr_2Cl_2	"	unchanged	"	+ traces of QmBr_2I_2	—
$\text{QmBr}_2\text{Br}_2 + \text{Cl}_2$	QmBr_2Br_2	"	QmBr_2Cl_2	QmBr_2Br_2	QmBr_2IBr	—
$\text{QmBr} + \text{I}_2$	QmBr_2I_2	unchanged	$\text{QmCl}_2\text{ICl}_2$	QmBr_2IBr	unchanged	—
$\text{QmI} + \text{I}_2$	QmI_2	"	$\text{QmCl}_2\text{ICl}_2 + \text{QmCl}_2\text{ICl}$	"	QmI_2 , etc.	—
$\text{QmI} + 2\text{I}_2$	QmI_2I_2	"	"	"	—	—

TABLE II.

Product when treated with			
Quant. ammon. salt.	Cl_2	Br_2	I_2
QmCl	—	—	—
QmBr	QmBr_2Cl_2	QmBr_2Br_2	QmBr_2I_2
QmI	QmI_2I_2	QmI_2	QmI_2

in derivatives of the quaternary ammonium bromide only when iodine is also present in the solution. The chlorine of iodine monochloride replaces the *N*-bromine of QmBr only when at least two atomic proportions of Cl (as ICl) are present. Chlorine replaces the added halogens in QmBr, Br₂ giving QmBr, Cl₂.

2. Bromine causes replacement of the *N*-halogen in the quaternary ammonium iodide and in periodides. Bromine replaces, to a very small extent, the *N*-halogen in the quaternary ammonium chloride, yielding perbromides. Bromine does not react with derivatives of the quaternary ammonium chloride such as QmCl, ICl₃ and QmCl, ICl.

3. Iodine was found to replace *N*-halogens in only one case, and then only to a small extent, that is, QmCl, treated with excess of iodine, gave a small quantity of the periodide. Iodine was found frequently to combine with the added halogens, forming iodine monochloride or monobromide (2 mols.); one molecule combined with the quaternary ammonium salt, forming a mixed perhaloid, so that the final result appeared as though one atom of added halogen had been replaced by iodine: $\text{QmBr, Br}_2 + \text{I}_2 = \text{QmBr, IBr} + \text{IBr}$.

The validity of these generalisations is exemplified by the following experiments :

(a) A hot solution of QmCl, ICl₃ and QmCl, ICl in glacial acetic acid was treated with bromine. The crystals which separated on cooling were found to be identical with the unchanged substance. This result supports generalisation 1, for if a perbromide were formed momentarily, being in presence of chlorine and iodine monochloride, it must reform immediately QmCl, ICl and QmCl, ICl₃.

(b) One molecular proportion of iodine trichloride was dissolved in glacial acetic acid and heated at 40° so as to become dissociated largely into chlorine and iodine monochloride. One molecular proportion of phenyltrimethylammonium bromide, also dissolved in glacial acetic acid, was added to the solution, when crystallisation began in less than a minute, the product being QmCl, ICl and not QmBr, ICl or QmBr, Cl₂.

(c) Acetic acid solutions of varying amounts of iodine monochloride, carefully purified by distillation so as to be free from the trichloride, were added to acetic acid solutions of phenyltrimethylammonium bromide. When one molecular proportion of iodine monochloride was used, the product was found to be QmBr, ICl, but when two or more molecular proportions were used, the product was invariably QmCl, ICl. In the latter case, the product was found to be the same irrespective of whether the bromide solution was added to the iodine monochloride or vice versa, provided at least

two molecular proportions of the monochloride were present before the mixed solutions were cooled and had begun to crystallise.

As perhaloids are in general much less soluble in acetic acid than the parent quaternary ammonium salts, it was considered likely that low solubility might be the determining factor in deciding which compound would result, but investigation showed that such is not a factor of the first order of importance in deciding the course of the reactions. This fact, taken in conjunction with the absence of isomeric forms, suggests that the course of the reaction depends entirely on the inherent stability of certain arrangements or groupings of halogen atoms.

The stability of the perhaloids has been studied from another point of view, namely, that of the dissociation pressure of the finely powdered solid under the influence of rise in temperature. The values obtained are given in the experimental portion. In spite of a few slight discrepancies, the order of these dissociation pressures for the perhaloids is surprisingly small, being less than those of the quaternary ammonium salts themselves up to temperatures of about 90° . Above this temperature, rapid decomposition takes place. This result, although unexpected, is not altogether without a parallel, for somewhat similar behaviour is noticeable in the case of corresponding oxygen compounds, for example, the relative stability of chlorates and hypochlorites.

EXPERIMENTAL.

Analysis has been found necessary only where either a new substance has been encountered or the identification of a compound by means of (a) appearance and crystalline form, (b) melting point, alone or in admixture, has been inconclusive. In general, much more reliance can be placed on these two simple methods than had been anticipated, although it will be appreciated that with such reactive substances as perhaloids the melting point of a mixture did not always give definite results owing to mutual interaction.

Analysis.—The halogen estimations were all done in sealed tubes at 240° . The mixed silver haloids were weighed and then converted into silver chloride by heating in a stream of chlorine at 200° .

Methods of Degradation.—(a) By means of Ethyl Malonate. As an example of this method, the degradation of $\text{NPhMe}_3\text{Cl}_2\text{ICl}_2$ may be described. The perhaloid was dissolved in about ten times its weight of ethyl malonate and warmed quickly to 40° , when evolution of hydrogen chloride began. The solution was then transferred to a desiccator and the latter evacuated. On the addition of ether to the solution the lower perhaloid was

precipitated in a pure condition, the yield being 97 per cent. of the theoretical. (b) By means of Acetone. For this method, absolutely dry acetone must be used. The best temperatures were found to be between 18° and the boiling point, and at the end of the reaction the quaternary ammonium salt usually crystallised from the reaction mixture or was precipitated by the addition of dry ether.

Action of Halogens on Phenyltrimethylammonium Iodide.—Chlorine in glacial acetic acid at 20 – 80° gave a mixture of $\text{NPhMe}_3\text{Cl}, \text{ICl}_3$ (2 mols.) and $\text{NPhMe}_3\text{Cl}, \text{ICl}$ (1 mol.). Bromine at 80° in glacial acetic acid yielded $\text{NPhMe}_3\text{Br}, \text{IBr}$, whilst iodine at 80° yielded the di-, tetra-, and hexa-iodides. Iodine monochloride at 100° in glacial acetic acid gave $\text{NPhMe}_3\text{I}, \text{I}_4$ (60 per cent. yield).

Phenyltrimethylammonium Bromide, NPhMe_3Br .—This was prepared by a modification of the method employed by Vorländer and Siebert (*Ber.*, 1919, 52, 284) and by Tapel and Brendler (*Ber.*, 1898, 31, 1349). Fifty grams of $\text{NPhMe}_3\text{Br}, \text{Br}_2$, prepared from the sulphate by the addition of bromine, were dissolved in 150 c.c. of dry acetone and shaken. After five minutes, the solution became colourless and precipitation of the quaternary bromide took place. This was recrystallised from a mixture of dry alcohol and dry ether. The yield was 32 grams.

With chlorine at 60° in glacial acetic acid, the quaternary ammonium bromide gave $\text{NPhMe}_3\text{Br}, \text{Cl}_2$ (Found : C = 37.7; H = 5.0; Br = 27.8; Cl = 24.1. $\text{C}_9\text{H}_{14}\text{NCl}_2\text{Br}$ requires C = 37.7; H = 4.9; Br = 27.85; Cl = 24.7 per cent.); with bromine, it gave $\text{NPhMe}_3\text{Br}, \text{Br}_2$, with iodine, $\text{NPhMe}_3\text{Br}, \text{I}_2$, with iodine monobromide $\text{NPhMe}_3\text{Br}, \text{IBr}$, with iodine monochloride (1 mol.), $\text{NPhMe}_3\text{Br}, \text{ICl}$, and with iodine trichloride or the monochloride (2 mols.), there resulted $\text{NPhMe}_3\text{Cl}, \text{ICl}$.

Phenyltrimethylammonium Chloride, NPhMe_3Cl .—This could not be isolated in the solid form, but was obtained as an oil when the hydroxide and hydrochloric acid were concentrated to a syrup, the syrup dissolved in absolute alcohol, and the chloride precipitated by ether. For identification purposes, the double salt with mercuric chloride, $\text{NPhMe}_3\text{Cl}, \text{HgCl}_2$, melting at 184° , was employed. Chlorine, dissolved in hydrochloric acid, in alcohol, or in glacial acetic acid, had no action on this compound; bromine gave a 10 per cent. yield of $\text{NPhMe}_3\text{Br}, \text{Br}_2$; iodine in acetic acid gave a 10 per cent. yield of the tetra-iodide, $\text{NPhMe}_3\text{I}, \text{I}_4$ (m. p. 84°); whilst iodine monochloride gave a nearly quantitative yield of $\text{NPhMe}_3\text{Cl}, \text{ICl}$.

Action of Halogens on Phenyltrimethylammonium Iodide Di-iodide and on the Tetra-iodide.—The di-iodide, $\text{NPhMe}_3\text{I}, \text{I}_2$, when treated

with chlorine in glacial acetic acid at 45° , gave $\text{NPhMe}_3\text{Cl}_2\text{I}$, melting at 144° , whilst bromine at 80° gave $\text{NPhMe}_3\text{Br}_2\text{I}$, melting at 120° ; iodine gave the tetra-iodide, NPhMe_3I_4 .

The tetra-iodide with chlorine at 100° gave a mixture of $\text{NPhMe}_3\text{Cl}_2\text{I}$ and $\text{NPhMe}_3\text{Cl}_2\text{I}_2$.

Phenyltrimethylammonium Bromide Dichloride, $\text{NPhMe}_3\text{Br}_2\text{Cl}_2$.—This substance could be obtained by the direct action of chlorine on the quaternary ammonium bromide, but was prepared best by chlorinating phenyltrimethylammonium bromide dibromide, $\text{NPhMe}_3\text{Br}_2\text{Br}_2$, in glacial acetic acid at 80° . The *dichloride* was precipitated by the addition of ether and when recrystallised from glacial acetic acid, in which it is somewhat easily soluble, it formed very pale yellow leaflets which melted at 111° (Found: C = 37.7; H = 5.0; Cl = 24.1; Br = 27.8. $\text{C}_9\text{H}_{14}\text{NCl}_2\text{Br}$ requires C = 37.7; H = 4.9; Cl = 24.7; Br = 27.85 per cent.). The constitution of this substance was established by its losing chlorine when kept in a vacuum desiccator over potassium hydroxide and also by its decomposition in the cold by acetone, when the quaternary bromide was produced (Found: Br = 36.7. Calc., Br = 37.0 per cent.).

Chlorine was without further action on the dichloride, and bromine at 60° in glacial acetic acid had no action. Iodine in acetic acid at the boiling point gave $\text{NPhMe}_3\text{Cl}_2\text{I}$.

Phenyltrimethylammonium Bromide Iodochloride, $\text{NPhMe}_3\text{Br}_2\text{I}_2\text{Cl}$.—This was prepared by heating together in glacial acetic acid for five minutes equivalent quantities of iodine monochloride and phenyltrimethylammonium bromide. When the solution was cooled, sandy-yellow crystals separated, which, after two crystallisations from glacial acetic acid, melted at 104° . The yield was 80 per cent. of the theoretical (0.2902 gave 0.4300 of mixed silver haloids, which yielded after chlorination the ratio silver haloids/ AgCl = 1.33. $\text{C}_9\text{H}_{14}\text{NClBrI}$ requires 0.434 mixed haloids and the ratio 1.316). The constitution of this substance was established by treatment with acetone, which yielded the quaternary ammonium bromide free from chloride or iodide.

This iodochloride, when treated with chlorine at 90° , gave $\text{NPhMe}_3\text{Cl}_2\text{I}_2$; bromine was without action on it; whilst iodine gave traces of $\text{NPhMe}_3\text{Br}_2\text{I}_2$.

Phenyltrimethylammonium Bromide Iodobromide, $\text{NPhMe}_3\text{Br}_2\text{IBr}$.—This substance was formed by the action of bromine on $\text{NPhMe}_3\text{Br}_2\text{I}_2$ or $\text{NPhMe}_3\text{I}_2\text{I}_2$, by the action of iodine on $\text{NPhMe}_3\text{Br}_2\text{Br}_2$, or by the action of iodine bromide on NPhMe_3Br . The best method of preparation consisted in the addition of a slight excess of bromine to an acetic acid solution of phenyltrimethyl-

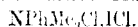
ammonium iodide at 60° . The yield was nearly theoretical and the product, when recrystallised from glacial acetic acid, consisted of glistening orange plates which melted at 120° (Found : Br = 38.1; I = 29.1; N = 3.21. $C_9H_{14}NBr_2I$ requires Br = 37.8; I = 29.9; N = 3.3 per cent.). The constitution of this substance was established by treatment with acetone, when the quaternary ammonium bromide resulted. Chlorine acted on this iodobromide to produce a 96 per cent. yield of $NPhMe_3Cl,ICl_3$, whilst bromine was without action on it, and iodine gave only traces of $NPhMe_3Br,I_2$.

Phenyltrimethylammonium Bromide Di-iodide, $NPhMe_3Br,I_2$.—This compound was prepared by the addition of the calculated weight of iodine to a concentrated solution of the quaternary ammonium bromide in acetic acid. The mixture was kept at 100° for a few minutes, and, on cooling, the di-iodide separated. It was recrystallised from glacial acetic acid, when it formed deep orange-brown plates melting at 114° . The yield was about 83 per cent. of the theoretical (Found : Br = 16.1; I = 55.2. $C_9H_{14}NBrI_2$ requires Br = 17.4; I = 55.2 per cent.).

The constitution was inferred from its method of preparation and from the fact that it resembled the periodides in not being degraded by treatment with acetone.

When chlorine was passed into a solution of the di-iodide in glacial acetic acid, bromine was evolved and $NPhMe_3Cl,ICl_3$ separated. Bromine acted on the di-iodide and produced $NPhMe_3Br,IBr$, whilst iodine was without further action.

Phenyltrimethylammonium Chloride Iodomonochloride,



This compound was originally prepared by Samtleben (*Ber.*, 1898, **31**, 1146), who obtained it by the action of chlorine on phenyltrimethylammonium iodide in hydrochloric acid solution. It can be obtained also by the action of ethyl malonate at 40° on $NPhMe_3Cl,ICl_3$, or by the action of iodine on $NPhMe_3Br,Cl$.

Samtleben's suggestion that this substance was the iodochloride of the quaternary ammonium chloride has been confirmed by means of degradation with acetone and the conversion of the very soluble chloride produced into the double salt with mercuric chloride, $NPhMe_3Cl,HgCl_2$, which melts at 184° . It was found possible also to synthesise the compound from the quaternary chloride and iodine monochloride in acetic acid solution.

The action of chlorine on the iodomonochloride converted it partly into the iodotrichloride, $NPhMe_3Cl,ICl_3$, which usually crystallised along with the unchanged monochloride. Bromine and iodine were without action on the substance.

Phenyltrimethylammonium Chloride Iodotrichloride, $\text{NPhMe}_3\text{Cl}_2\text{I}$.—The best method for the preparation of this substance consisted in the action of chlorine on a glacial acetic acid solution of $\text{NPhMe}_3\text{Br}_2\text{I}$ at $60\text{--}70^\circ$. When the solution was cooled, the product crystallised in long, yellow needles which melted at 144° . It can also be prepared by chlorination of the periodide (0.3225 gave 0.6461 of mixed silver haloids, which after chlorination gave mixed haloids/ $\text{AgCl} = 1.129$. $\text{C}_9\text{H}_{14}\text{NCl}_4\text{I}$ requires 0.6450 of mixed haloids and the ratio 1.128).

This product was also formed together with the iodomonochloride by the chlorination of phenyltrimethylammonium iodide in glacial acetic acid at any temperature between 20° and 100° . The two products were separated by dissolving 3 grams in 60 c.c. of glacial acetic acid at $104\text{--}106^\circ$ and allowing the solution to cool slowly, when both products crystallised and could be separated by hand-picking with the aid of a lens; the addition of a few drops of bromine facilitated this separation by tinting the crystals to a different degree. For a long time the product of chlorination, which melts at 141° , was thought to be homogeneous and to have the formula $(\text{NPhMe}_3\text{Cl}_2\text{I})_2$, $\text{NPhMe}_3\text{Cl}_2\text{I}$ (Found: $\text{C} = 28.3$; $\text{H} = 3.8$; $\text{N} = 3.6$; $\text{Cl} = 30.9$; $\text{I} = 33.7$. Calc., $\text{C} = 28.3$; $\text{H} = 3.7$; $\text{N} = 3.7$; $\text{Cl} = 31.0$; $\text{I} = 33.3$ per cent.). It is best regarded as a double salt.

The constitution of the iodotrichloride is established by (a) treatment with ethyl malonate, when the iodomonochloride results, and (b) treatment with acetone and the addition of mercuric chloride, when the characteristic double salt derived from the quaternary ammonium chloride is precipitated. Further, it was possible to synthesise this substance by the action of iodine trichloride on the quaternary ammonium chloride and separation of the two constituents of the double salt.

Chlorine and bromine were found to be without action on the iodotrichloride. On grinding the substance with water, a red colour was formed immediately, and on standing a small quantity of NPhMe_3I_2 was precipitated. When the substance was treated with a concentrated aqueous solution of potassium hydroxide and the solution acidified with acetic acid, a small quantity of the same periodide was produced.

Solubilities of the Perhaloids in Acetic Acid at 38° .

Perhaloid.	Solubility in grams per litre.	Relative solubility in mols.	Perhaloid.	Solubility in grams per litre.	Relative solubility in mols.
$\text{NPhMe}_3\text{Br}_2\text{Cl}_2$	50	35.1	$\text{NPhMe}_3\text{Br}_2\text{I}$	6.6	3.1
$\text{NPhMe}_3\text{Br}_2\text{Br}_2$	8	4.6	$\text{NPhMe}_3\text{Cl}_2\text{I}$	13.3	8.0
$\text{NPhMe}_3\text{Br}_2\text{I}$	6.5	2.8	NPhMe_2I_2	4.0	1.6

Vapour Pressures of the Perhaloids at Different Temperatures.

The apparatus used consisted of two small similar distilling flasks, to the side tubes of which were fused the two upper ends of a long narrow U-tube, fitted with small bulbs at the upper end of each limb. The U-tube, partly filled with mercury, acted as a manometer. The dried, finely powdered substances to be compared were introduced into the distilling flasks, the neck of one flask was sealed whilst the other distilling flask was connected with a pump, completely evacuated, and sealed. The bulbs of the flasks were immersed in a thermostat, and readings were taken at each temperature. A simpler form of the apparatus was made by fusing together a single distilling flask and a U-tube with a very long sealed limb. With this apparatus the absolute dissociation pressures of the substances were obtained directly.

Substance.	M. p.	Vapour pressures in mm. of mercury at						
		38°.	60°.	80°.	89°.	94—96°.	100°.	155°.
QmBr	214°	6	21	—	54	62		
QmBr.Br ₂	112	—	5.5	5.5	6	>322		
QmBr.Cl ₂	111	11	13	16.5	9(?)	—		
QmBr.I ₂	114	2.5	3	4	—	6	6.5	15
QmI	224	2	5	8	8.5	11		
QmI.I ₂	116	—	2	1	—	2	1.5	>170
QmI.I ₂	86	1.5	3	4	—	5		
QmCl.ICl ₃	144	1	1	—	—	10		

Summary.

The preparation and properties of the following new perhaloids are described: NPhMe₃Cl₂ICl₃; NPhMe₃Br₂Cl₂; NPhMe₃Br₂IBr; NPhMe₃Br₂I₂; NPhMe₃Br₂ICl.

The results of chlorination, bromination, and iodination of each of the following are also described: (NPhMe₃)₂SO₄; NPhMe₃NO₃; NPhMe₃Cl; NPhMe₃Cl₂ICl; NPhMe₃Cl₂ICl₃; NPhMe₃Br; NPhMe₃Br₂Cl₂; NPhMe₃Br₂Br₂; NPhMe₃Br₂I₂; NPhMe₃Br₂I₂; NPhMe₃Br₂ICl; NPhMe₃Br₂ICl₃; NPhMe₃Br₂IBr; NPhMe₃I; NPhMe₃I₂; NPhMe₃I₂I₄.

The following deductions have been drawn from these results.

1. Since the sulphate and nitrate do not give stable perhaloids, perhaloid formation is due to the halogen of the quaternary ammonium salt and not to the nitrogen atom.

2. The bromide gives the widest range of stable perhaloids by direct addition.

3. Chlorine always replaces the *N*-halogen if iodine is also present.

4. In the absence of iodine, chlorine replaces the added halogen, not the *N*-halogen.

5. Bromine replaces *N*-iodine, but not *N*-chlorine or added chlorine to any appreciable extent.

6. Up to 95°, the perhaloids have smaller vapour pressures than the parent quaternary ammonium salts.

7. Low solubility is insufficient to explain these reactions.

8. The assumption that these perhaloids are molecular compounds fails in a similar manner.

9. True chemical affinity where the halogens are multivalent is the only explanation of these experiments.

10. Two methods of determining the constitution of the perhaloids by the successive removal of the most easily detached halogens by means of (a) ethyl malonate under reduced pressure and (b) acetone are given.

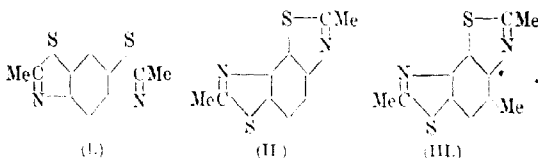
CHEMISTRY DEPARTMENT,

THE UNIVERSITY, CAMBRIDGE. [Received, September 20th, 1922.]

XVIII.—Benzbisthiazoles. Part II.

By STEPHEN RATHBONE HOLDEN EDGE.

A PREVIOUS paper (Edge, T., 1922, 121, 772) described the preparation of a benzbisthiazole from *m*-phenylenediamine. This benzbisthiazole was there regarded as being probably 2:6-dimethylbenzbisthiazole (I), although it could theoretically be 2:7-dimethylbenzisobisthiazole (II). To help to elucidate this point, a benzisobisthiazole, 2:4:7-trimethylbenzisobisthiazole (III) has been prepared starting from *m*-tolylenediamine.



The method was similar to that employed before, the acetyl derivative of the diamine being converted into a mixture of thioacetyl derivatives and this oxidised in alkaline solution to the bisthiazole. The oxidation to bisthiazole did not go as smoothly as before—more tarry matter was produced and yields of pure product were very small. Just as in the previous case, a mixture of constant composition and sharp melting point of seven molecules of dithioacetyl-*m*-tolylenediamine with two molecules of monothiodiacetyl-*m*-tolylenediamine was discovered. From this, pure dithioacetyl-*m*-

tolylenediamine was obtained after very many recrystallisations from water. The monothio-compound appears in this case to be tarry and could not be isolated.

This trimethylbenzisobisthiazole is a much weaker base than the previously described dimethylbenzbisthiazole. Its monohydrochloride is decomposed by boiling water with production of an emulsion of the bisthiazole. When dry, the hydrochloride begins to decompose below 100° and for this reason has no definite melting point. The thiazole dissolves in concentrated hydrochloric acid and the solution appears stable. On diluting slightly, the monohydrochloride is precipitated. On further dilution this precipitate redissolves.

Definite evidence of the existence of a dimethiodide was obtained. This somewhat surprising fact provides an explanation of the high iodine content found for the monomethiodide of the 2:6-dimethylbenzbisthiazole previously prepared. The method of production of the bisthiazole might be expected to give small quantities of the isomeric 2:7-dimethylbenzisobisthiazole in addition to the main bulk of 2:6-dimethylbenzbisthiazole. If now *benzisobisthiazole* is a diacid base and gives a dimethiodide, the high iodine content is explained. Working on this hypothesis, it was noticed that the specimen of the bisthiazole which had been recrystallised seven or eight times to get a sharp and constant melting point had never been used for making the methiodide. On carrying out the preparation and analysis of the methiodide with a little of this sample, the value $I = 34.92$ was obtained, theory requiring $I = 35.09$ per cent. for the monomethiodide. Since there can be no doubt as to the structure of the trimethylbenzisobisthiazole now prepared, and since the dimethylbenzbisthiazole previously described shows no trace of being a diacid base, the above results point definitely to its being 2:6-dimethylbenzbisthiazole.

EXPERIMENTAL.

Mixture of Mono- and Di-thioacetyl-m-tolylenediamines.—Fifty grams of diacetyl-*m*-tolylenediamine and 25 grams of finely-powdered phosphorus pentasulphide boiled under reflux with 500 c.c. of toluene for one and a half hours, yielded on treatment just as before described 35–38 grams of the crude mixture. Three recrystallisations from alcohol brought the melting point of this product up to 178° , at which it remained constant after further recrystallisation from alcohol. This mixture of constant m. p. consists of a yellowish-white powder of minute, needle-shaped crystals. The melting point is raised and made much less sharp by mixing with pure dithioacetyl-*m*-tolylenediamine (Found:

$S = 24.04$. Calc. for 7 mols. of dithio- to 2 mols. of monothioacetyl derivative, $S = 24.27$ per cent.).

Dithioacetyl-m-tolylenediamine.—Repeated crystallisation of the above mixture from water slowly raised its melting point to $185-186^\circ$, at which point it became constant. Fine, yellowish-white, needle-shaped crystals were obtained (Found: $C = 55.93$; $H = 5.98$; $S = 27.16$. Calc., $C = 55.46$; $H = 5.88$; $S = 26.90$ per cent.).

2:4:7-Trimethylbenzisobisthiazole.—A solution of 20 grams of crude dithioacetyl-*m*-tolylenediamine and 68 grams of sodium hydroxide in 500 c.c. of water is added to 180 grams of commercial potassium ferricyanide in 1000 c.c. of water. After keeping for one hour, the precipitate is collected and dissolved in 250 c.c. of alcohol, the solution, diluted to 500 c.c. with water, is boiled with animal charcoal, filtered, cooled, just acidified with dilute hydrochloric acid, and the precipitated tar removed. The solution is made strongly alkaline (80 grams of sodium hydroxide) and extracted with ether. The ethereal solution is dried with sodium sulphate, boiled with charcoal, and filtered. The residue left after evaporation of the ether is crystallised from hot light petroleum, when the *bisthiazole* (yield about 2 grams) is obtained in white, feathery needles, m. p. $115-116^\circ$ (Found: $C = 56.73$; $H = 4.02$; $S = 27.45$. $C_{11}H_{10}N_2S_2$ requires $C = 56.41$; $H = 4.27$; $S = 27.35$ per cent.). The *hydrochloride*, made by dissolving the *bisthiazole* in concentrated hydrochloric acid, diluting slightly, and filtering off the copious white precipitate, forms very minute, needle-shaped crystals, which melt and decompose at $170-180^\circ$ (Found: $Cl = 13.22$. $C_{11}H_{10}N_2S_2.HCl$ requires $Cl = 13.12$ per cent.).

Methiodides.—Approximately 0.15 gram of the *isobisthiazole* was heated with excess of methyl iodide for several hours in a sealed tube. After drying in air until no further loss in weight occurred, the increase in weight was found to be 0.16 gram (roughly, theory requires an increase of 0.09 gram for the monomethiodide and of 0.19 gram for the dimethiodide).

0.5 Gram was heated with methyl iodide as before, and the product, recrystallised from water, gave white, matted crystals. These were dried at 100° . From the appearance it was obvious that some decomposition had taken place (Found: $I = 28.89$ per cent.).

The above experiment was repeated, care being taken to heat for as short a time as possible when recrystallising, and the air-dried product was dried in a vacuum desiccator without further heating (Found: $I = 46.00$. Theory requires, for the monomethiodide, $I = 33.78$; for the dimethiodide, $I = 49.04$ per cent.).

Lack of material prevented further repetitions of the above preparation. No definite melting points could be obtained because of the decomposition which started even below 100°.

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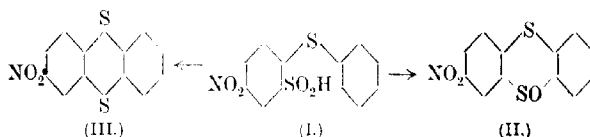
[Received, December 13th, 1922.]

XIX.—*Synthesis of Substituted Thianthrens. Part I.* *Thianthren and Nitrothianthren.*

By SRI KRISHNA.

PERUSAL of the literature on substituted thianthrens shows that the methods of preparation hitherto described give only the symmetrically disubstituted derivatives and are applicable only in a very limited number of cases (see, for example, Fries and Volk, *Ber.*, 1909, **42**, 1170; Fries and Engelbertz, *Annalen*, 1915, **407**, 194; Cohen and Skirrow, *T.*, 1899, **75**, 888; Rây, *T.*, 1921, **119**, 1962).

An attempt is now being made to synthesise mono-, di-, or poly-substituted thianthrens by a method that should be applicable to benzene derivatives containing acid or basic substituents. The present communication describes the synthesis of thianthren by a method which utilises the reactivity of the halogen atom in negatively substituted chlorobenzene. 6-Chloro-3-nitrobenzenesulphinic acid condenses with the sodium derivative of phenyl mercaptan, 4-nitro-2-sulphinodiphenyl sulphide (I) being formed. This is readily soluble in concentrated sulphuric acid. If the blue solution



obtained is immediately diluted with water, the sulphoxide (II) will be precipitated, but if the solution is kept for half an hour before dilution, 3-nitrothianthren (III) will be obtained and sulphur dioxide evolved.

3-Nitrothianthren is readily reduced to 3-aminothianthren, from which through the diazo-compound thianthren is obtained.

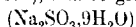
The *mono-* and the *di-sulphoxide* and the *disulphone* of 3-nitrothianthren have been prepared. The former dissolve in sulphuric acid, giving red and yellow solutions, but the disulphone forms a colourless solution.

A blue colour is produced when a solution of 3-nitrothianthren in glacial acetic acid is treated with hydrogen chloride or stannic chloride. The production of this blue colour has been regarded as evidence of the existence of quinonoid dithionium salts (Fries, *loc. cit.*). Attempts have been made to isolate such salts of 3-nitrothianthren, but these have not been successful due probably to the influence of a nitro-group. If 3-nitrothianthren is heated with anhydrous ferric chloride in acetic acid, a *ferrichloride* is formed. A dichloro-additive product is formed when dry chlorine is passed into a glacial acetic acid solution of 3-nitrothianthren, but attempts to isolate the substance have failed, as it is very quickly converted into a sulphoxide in presence of moisture.

The present work is interesting because the starting material contains a nitro-group, the presence of which in the molecule has been found to inhibit the course of other methods of synthesis (Rây, *loc. cit.*). Several mercaptans, containing various substituents, have been condensed in the above fashion and the reaction has so far been found to be a general one. Experiments are in progress to synthesise thianthrens containing hydroxy-, nitro-, or sulpho-groups, the preparation of which has defied all attempts made by previous workers.

EXPERIMENTAL.

6-Chloro-3-nitrobenzenesulphinic Acid.—A mixture of 20 grams of 6-chloro-3-nitrobenzenesulphonyl chloride, prepared by Fischer's method (*Ber.*, 1891, **24**, 3194), and 50 grams of sodium sulphite



in 75 c.c. of water was shaken for three hours, until the sulphonyl chloride had dissolved. The mixture was tested for alkalinity from time to time and dilute sodium hydroxide was added to prevent formation of sulphur dioxide. The mixture was kept at atmospheric temperature by the addition of ice, any undue increase of temperature being fatal to the success of the experiment on account of hydrolysis of the sulphonyl chloride. The mixture was filtered, well cooled in ice, and concentrated hydrochloric acid slowly added, when a crystalline solid separated. The *sulphinic acid* crystallises from water in shining, colourless plates, m. p. 139°. It gives the usual test with concentrated sulphuric acid and phenetole (Found: Cl = 16.15; S = 14.68. $\text{C}_6\text{H}_4\text{O}_4\text{NClS}$ requires Cl = 16.02; S = 14.44 per cent.).

4-Nitro-2-sulphinodiphenyl Sulphide (Formula I).—A solution of 22 grams of 6-chloro-3-nitrobenzenesulphinic acid in 50 c.c. of water, containing 4 grams of sodium hydroxide, was added to a boiling solution of 11 grams of phenyl mercaptan in 25 c.c. of water, containing

4 grams of sodium hydroxide, during twenty minutes, during which time the temperature of the boiling solution rose to 105–107°. The red solution, when cold, was filtered, diluted to about 300 c.c. with ice and water, and slowly acidified with cold dilute sulphuric acid, a yellow, crystalline product being obtained. If the acid had been added too quickly, the deposit was oily; it hardened, however, on keeping. The product sometimes contained phenyl mercaptan (in which case the precipitate was invariably soft), and this was removed by grinding with ether. The 4-nitro-2-sulphinodiphenyl sulphide, when dry, was crystallised from chloroform or alcohol in very small, lemon-yellow needles, m. p. 135°. This substance is very soluble in cold dilute alkalis (Found: C = 49.12; H = 3.26; S = 22.05; N = 4.60. $C_{12}H_9O_1NS_2$ requires C = 48.81; H = 3.05; S = 21.76; N = 4.74 per cent.).

3-Nitrothianthren (Formula III).—The preceding sulphinic acid was finely powdered and dissolved by addition in small portions to a convenient volume of concentrated sulphuric acid at room temperature (20 grams of the sulphinic acid usually required 75 c.c. of the mineral acid). The solution, the red colour of which changed to violet-blue on keeping, was poured after twenty to twenty-five minutes into 500 c.c. of water, when a dull yellow solid separated. This was collected, washed several times with hot water, dried, and crystallised from formic acid, when 3-nitrothianthren was obtained in small, orange needles, m. p. 128°. It can be distilled in a vacuum at 260° and sublimes in long, slender, orange needles. It is quite insoluble in boiling alkalis, but dissolves in strong sulphuric acid giving a deep violet solution, from which it is reprecipitated unchanged on the addition of water (Found: C = 55.31; H = 2.89; S = 24.33; N = 5.51. $C_{12}H_7O_2NS_2$ requires C = 55.17; H = 2.70; S = 24.13; N = 5.36 per cent.).

3-Aminothianthren, $NH_2 \cdot C_6H_3 \begin{smallmatrix} \diagup N \\ \diagdown \end{smallmatrix} C_6H_4$.—Ten grams of 3-nitrothianthren, dissolved in 60 c.c. of 90 per cent. acetic acid, were reduced by boiling under reflux for three to four hours with zinc dust. The cooled mixture was filtered and poured into a large volume of water, when a voluminous, white precipitate appeared. This having been well washed, and warmed with strong aqueous ammonia several times to remove traces of acetic acid, the product was dried and crystallised from acetone or alcohol, being obtained in colourless needles, m. p. 185° (Found: N = 6.26; S = 27.82. $C_{12}H_9NS_2$ requires N = 6.06; S = 27.70 per cent.).

3-Aminothianthren dissolves in concentrated sulphuric acid forming a deep blue solution. The hydrochloride and the sulphate, which are quite easily prepared, are only slightly soluble in water

but fairly soluble in dilute alcohol. These salts are readily diazotised by the usual methods; the diazotised solutions give bright red precipitates with alkaline solutions of β -naphthol and resorcinol.

Thianthren.—To a boiling solution of 7 grams of 3-aminothianthren in 50 c.c. of absolute alcohol and 6 grams of concentrated sulphuric acid, 1.5 grams of sodium nitrite were added in small portions. After two hours' boiling, the solution was filtered into 300 c.c. of water, when a white precipitate separated. This was collected, washed, dried, and crystallised from alcohol. The product thus obtained sublimed in a vacuum in long needles, which were identified as thianthren by the melting point of its mixture with a genuine sample.

3-Nitrothianthren Monoxide (Formula II).—This compound was obtained when 4-nitro-2-sulphinodiphenyl sulphide was dissolved in concentrated sulphuric acid at about 50°. The method of isolating the product was the same as that described in the case of 3-nitrothianthren. The sulphoxide was also prepared by boiling an acetic acid solution of 3-nitrothianthren with dilute nitric acid for one hour. The cooled mixture was poured into water, and the sulphoxide was crystallised from dilute acetic acid in nodules, m. p. 166°. It was reduced to 3-nitrothianthren by boiling with hydrogen bromide in acetic acid solution. It dissolved in concentrated sulphuric acid with a red colour and was reprecipitated unchanged with water (Found : $S = 23.15$. $C_{12}H_7O_3NS_2$ requires $S = 23.10$ per cent.).

3-Nitrothianthren Dioxide, $NO_2 \cdot C_6H_3 \begin{smallmatrix} \text{SO} \\ \text{SO} \end{smallmatrix} > C_6H_4$, was prepared by oxidising 3-nitrothianthren in boiling glacial acetic acid with nitric acid ($d\ 1.4$). After boiling for half an hour, the mixture was poured into water, and the light yellow (sometimes cream-coloured) precipitate was collected, washed, dried, and crystallised from dilute acetic acid, forming light brown prisms, m. p. 226° (Found : $S = 21.98$. $C_{12}H_7O_4NS_2$ requires $S = 21.84$ per cent.).

3-Nitrothianthren Tetroxide, $NO_2 \cdot C_6H_3 \begin{smallmatrix} \text{SO}_2 \\ \text{SO}_2 \end{smallmatrix} > C_6H_4$.—This disulphone was obtained when a hot glacial acetic acid solution of 3-nitrothianthren was added drop by drop to a boiling acetic acid solution of chromic acid. The product was isolated as described in the case of the sulphoxides, and crystallised from alcohol or dilute acetic acid in colourless prisms, m. p. 255° (Found : $S = 19.90$; $N = 4.24$. $C_{12}H_7O_6NS_2$ requires $S = 19.69$; $N = 4.30$ per cent.).

3-Nitrothianthren Ferrichloride, $2NO_2 \cdot C_6H_3 \begin{smallmatrix} \text{S} \\ \text{S} \end{smallmatrix} > C_6H_4 \cdot FeCl_3$, was prepared from anhydrous ferric chloride and 3-nitrothianthren in glacial acetic acid. On cooling the filtered mixture, dark brown

crystals of the double salt were obtained. These, recrystallised from acetic acid, melted at 223° (Found : Fe = 10.40. $2\text{C}_{12}\text{H}_7\text{O}_4\text{NS}_2$ requires Fe = 10.52 per cent.).

In conclusion, I desire to express my thanks to Professor Smiles, F.R.S., for his interest and helpful suggestions, and to the Research Fund Committee of the Chemical Society for the grant which defrayed part of the expenses incurred in this research.

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[Received, November 27th, 1922.]

XX.—*The Determination of the Dissociation Pressures of Hydrated Salts by a Dynamical Method. Part II.*

By JAMES RIDDICK PARTINGTON and DONALD BENNETT
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THE methods employed in the measurement of the dissociation pressures are (a) statical, (b) dynamical (Partington, T., 1911, 99, 467), (c) indirect. In the last method, water is removed by allowing the higher hydrate to come to equilibrium in a liquid, in which the hydrates are insoluble, or very slightly soluble. The amount of water in the liquid phase is then determined, and from this the dissociation pressure obtained.

Menzies (*J. Amer. Chem. Soc.*, 1920, 42, 1952) finds that considerable pressures, due to permanent gases, develop in tensimeters after exhaustion, and suggests that the abnormally high pressure, noticed by Schottky (*Z. physikal. Chem.*, 1908, 64, 433) during the initial stages of an experiment, is due to this cause. The pressures on each side, due to these gases, then become equalised by the dissolution and diffusion of the air, etc., in the oil.

Menzies determined the pressure of this residual air in the tensimeter after equilibrium had been reached by immersing the bulb, containing the salt, in a freezing mixture at -50° , and found a pressure of 0.3 mm. of mercury. He concludes that this is due to the persistence of the air during evacuation as an adsorbed layer on the crystals of the salt.

Wilson (*J. Amer. Chem. Soc.*, 1921, 43, 704) employed a small balance inside a desiccator, equipped with a fan and stirrer, and containing sulphuric acid solution, the strength of which was varied until the concentration was found at which the salt neither gained nor lost in weight, when exposed to the air in equilibrium with the acid. From the density of the acid the dissociation pressure of the

salt can be determined. The closeness of the limits between which the salt lost or gained in weight depended on the rate at which the salt gained or lost water. This is slow in the case of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O} \rightarrow \text{CuSO}_4 \cdot 3\text{H}_2\text{O}$, whilst in the cases of $\text{CuSO}_4 \cdot 3\text{H}_2\text{O} \rightarrow \text{CuSO}_4 \cdot \text{H}_2\text{O}$ and $\text{BaCl}_2 \cdot 2\text{H}_2\text{O} \rightarrow \text{BaCl}_2$ it is so slow as to make this an unsatisfactory method. Each determination lasts several weeks. Wilson states that these results are less open to question than those of other methods, as equilibrium can be approached from either side.

Tammann (*Wied. Ann.*, 1888, **33**, 329) introduced the transpiration method, whereby a measured volume of dry air is aspirated over the salt, and the water vapour evolved collected in suitable drying tubes. He observed that dissociation pressures measured in this way are higher than those determined tensimetrically and ascribed the difference to the presence of traces of saturated solution, retained by the crystals.

Campbell (*Trans. Faraday Soc.*, 1915, **10**, 202) confirmed Regnault's (*Wied. Ann.*, 1845, **15**, 129) and Shaw's (*Phil. Trans.*, 1888, **179**, [A], 73) observations that liquids exert a lower vapour pressure in the presence of gases than in the presence of their own saturated vapours only. He adduced evidence which indicates that this lowering is related to the solvent power of the liquid, although the amount of dissolved gas is insufficient to account for the whole of the observed lowering. Violent agitation causes these differences to tend to disappear. Campbell gives the following values for the vapour pressure of water at 70° ; in a vacuum 233.8 mm.; in hydrogen 230.8 mm. According to Winckler (*Z. physikal. Chem.*, 1892, **9**, 171), 100 grams of water dissolve 0.031019 gram of hydrogen at 70° under a total pressure of 760 mm.

The lowering of the vapour pressure, according to Raoult's law, will therefore be $\Delta p = p_0 n/N = 234 \times 0.0001019 \times 2 \times 18/100 = 0.00215$ mm. The observed lowering is 3.0 mm. There is, however, another effect of the presence of an inert gas on the vapour pressure of a liquid not referred to by Campbell, and this tends to raise the vapour pressure to an extent approximately given by Pv/V , where P is the pressure of the gas, and v and V are the specific volumes of the liquid and vapour, respectively (see J. R. Partington, "Text-book of Thermodynamics," 1913, p. 200). For water at 70° , $v = 1$ c.c. (approx.), and $V = \frac{760}{234} \times \frac{22.3}{18} \times \frac{343}{273} \times 1,000 = 5060$ c.c., and therefore $\Delta p = Pv/V = 760/5060 = 0.15$ mm. of Hg. This would mask the very small effect of opposite sign, due to the Raoult effect. Thus it appears that theory requires a small (and measurable) increase of vapour pressure in the presence of a relatively insoluble inert gas rather than the diminution actually found by

experiment, and therefore the true cause of the latter has yet to be discovered.

Campbell suggests that Tammann's high results may be due to this lowering of the vapour pressure in the presence of gases. A recalculation made by Campbell, of Tammann's values leads to results in better agreement with the values determined by Frowein (*Z. physikal. Chem.*, 1887, **1**, 5). The latter, however, are too low, as was shown by Menzies (*J. Amer. Chem. Soc.*, 1920, **42**, 1955).

The transpiration method was improved by Partington (T., 1911, **99**, 466), who eliminated the troublesome corrections for changes of temperature and barometric pressure. Tammann's observation that the pressures obtained by this method are slightly higher than those obtained by the tensimetric method was confirmed. Partington suggested that the first product of dehydration is an unstable, probably amorphous, lower hydrate or anhydrous salt, which slowly passes into the stable form, the true equilibrium pressure being then reached.

Baker (*Ann. Reports*, 1912, **8**, 34) believes the abnormally high pressures are due to the occlusion of saturated solution in the crystals of the salt. If this were the complete explanation, the pressures as measured by the tensimetric method should depend on the size of the bulb available for the production of vapour. If this is small, the vapour will come into equilibrium with traces of solution, and a higher pressure will be recorded. With a larger bulb, all the solution will evaporate and a lower pressure, due to the efflorescence of the salt, will be obtained. Experiments to test this point would probably be of interest.

Rae (T., 1916, **109**, 1235) recorded some experiments on the period of induction, occurring at the commencement of dehydration of a salt. He states that—"It may well be that the vapour pressure of very small particles of copper sulphate trihydrate may be much greater than that of larger particles, and may approach that of the pentahydrate; if this is really the case, it is clear that the formation of these particles, and therefore the initial stages of the change from pentahydrate to trihydrate, will take place with great difficulty, until the particles of the latter have reached a certain size."

His assumption that the increase of vapour pressure is due, not to the unstable modification of the trihydrate first formed (as suggested by Partington), but simply to the fine state of subdivision of the trihydrate in its ordinary stable form is, however, certainly not to be inferred from the result obtained with small particles of a pure substance, which volatilises unchanged. In the first place, this analogy, the basis of Rae's theory, would not

explain the differences observed, as the sizes of the small crystals would be larger than those required to produce measurable differences in the vapour pressure of small drops. Moreover, the two cases are totally different. When a drop of liquid evaporates, the composition remains unchanged and the physical and chemical characters of the interface, *liquid/vapour*, remain constant; whereas, when a crystal of copper sulphate pentahydrate effloresces, the physical and chemical characters of the interface, *solid/vapour*, alter completely, and the pressure is constant only when *two* solid phases are present.

Rae's comment that Partington's interpretation of his results and the postulation of the intermediate formation of an unstable lower hydrate seem unnecessary, appears to be unconvincing. The lower initial values are also an experimental fact, not explained by Rae's hypothesis.

Baxter and Lansing (*J. Amer. Chem. Soc.*, 1915, **37**, 309), employing Tammann's original transpiration method, measured the dissociation pressures of several salts with great exactitude.

Menzies (*J. Amer. Chem. Soc.*, 1920, **42**, 978) suggests that there are errors in Tammann's and in Partington's experiments due to the asbestos and glass wool plugs, used by these investigators. He observes that no other investigators used glass wool plugs to filter air, assumed to be of 100 per cent. humidity. In the experiments approved by Menzies, saturators of the Kahlenberg type (*Science*, 1905, July 21st) were employed; in these the air is slowly drawn over the surface of the water, and not bubbled through it. It should be recalled that Tammann did not employ a water saturator, but measured the volume of air aspirated over the salt.

Menzies enclosed glass wool, previously treated with steam and dried in a current of air for ten minutes at 250°,* in a U-tube and aspirated air, saturated with water vapour, over it. At first, 13.9 per cent. of the total weight of water vapour was retained by the glass wool, but the value gradually fell to 0.79 per cent. This effect is considered later in the present communication.

Menzies (*J. Amer. Chem. Soc.*, 1920, **42**, 1951) notices that no correction was applied to eliminate the error, pointed out by Berkeley (*Nature*, 1915, **95**, 54), arising when the moist air, in equilibrium with the salt, has a smaller volume than the saturated air in equilibrium with the water; or for the change of pressure due

* Mr. W. G. Shilling (recent investigations in this laboratory) finds that the film of adsorbed moisture is only given up by glass surfaces at 370° and by silica at 800° in a current of dry air. The dry surface then shows little tendency to become recoated with a new film of moisture. Compare also Partington and Cant, *Phil. Mag.*, 1922, [vi], **53**, 371.

to the head of water in the saturator. Menzies determined the dissociation pressure of copper sulphate pentahydrate by a procedure similar to Partington's and also with a tensimeter. A mean value of 7.80 mm. was obtained by the dynamical method, agreeing fairly well with the value, 7.74 mm., determined tensimetrically. The difference is stated to be due to condensation of the water vapour before it reaches the drying tubes, a phenomenon first noticed by Berkeley and Hartley (*Phil. Trans.*, 1909, 209, [A], 177).

Foote and Scholes (*J. Amer. Chem. Soc.*, 1911, 33, 1309) determined the dissociation pressures of hydrated salts by an indirect method, namely, by shaking the salts with aqueous alcohol. The results obtained are very low.

Wilson (*ibid.*, 1921, 43, 704) used amyl alcohol and estimated the water content of the mixture from the conductivity of this solution, when saturated with potassium thiocyanate. Noyes and Westbrook (*ibid.*, 1921, 43, 726) also employed this method. From the results of their experiments and those of Wilson, mentioned previously, a curve connecting the dissociation pressures of the salt and the composition of the equilibrium amyl alcohol-water mixtures was plotted. The curve shows that the water content can be determined with a fair degree of accuracy in the case of salts, for which trustworthy results have been obtained by other methods.

With copper sulphate pentahydrate, the percentage of water in the equilibrium mixture is 1.3 ± 0.2 , and this error produces a variation in the dissociation pressure of 1.0 mm. of mercury.

It seems extremely unlikely that this method will give better results with salts such as barium chloride dihydrate, with which investigators have experienced difficulties. The initial part of the curve slopes rather steeply and this means that the water in the amyl alcohol-water mixture has to be determined very accurately. This seems to be the defect of the method, whilst the chief advantage is that equilibrium may be approached from either side.

EXPERIMENTAL.

The efficiency of various types of saturator was first investigated. It was found that the bubbler type gave the best results, and the use of other types was discontinued.

A bubble, similar to that used by Partington (T., 1911, 99, 467) was attached to a vessel carrying the trap (Fig. 2, *loc. cit.*) and the absorption tube, filled with pumice which had been boiled with sulphuric acid. The apparatus was set up in a large thermostat, electrically controlled, the temperature of which remained constant within $\pm 0.002^\circ$, as indicated by a Beckmann thermometer. The bubbler with its trap and absorption tube was connected with a large aspirat-

ing bottle to which a mercury manometer was fitted, and air was drawn through the bubbler. The manometric and the barometric pressures and the temperature of the issuing water were noted every hour. When an experiment was finished, the taps were closed, and the absorption apparatus was detached, cleansed from the lubricant, vaselin, by means of cotton wool moistened with ether, and weighed against vessels of approximately the same volume and surface area. The air was initially dried by calcium chloride, and any water vapour was prevented from reaching the last absorption tube by a similar tube of calcium chloride, connected with the aspirating bottle.

The vapour pressure of water at 25° was found to be 23.80 mm. of mercury; Scheel and Heuse give 23.76 mm. (Landolt, Börnstein, and Meyerhoffer, "Tabellen," 4th edit., p. 360).

A plug of unwashed glass wool, dried at 110°, was now inserted in the tube between the bubbler and the trap, and the weight of water vapour per litre of saturated air determined as before.

Gram of water collected.	Volume (litres) of saturated air at 760 mm. and 25°.	Gram of aqueous vapour per litre.
0.2816	12.43	0.02185
0.1860	8.175	0.02273
0.2042	8.986	0.02273
Saturation value, found above		0.02285

Glass wool was boiled with water for twenty minutes, dried at 110°, and left in a desiccator over calcium chloride until the next morning, when it was placed in the apparatus and the experiments were continued.

Gram of water collected.	Volume (litres) of saturated air at 760 mm. and 25°.	Gram of aqueous vapour per litre.
0.2276	10.22	0.02227
0.1394	6.233	0.02237
0.0936	4.257	0.02252
0.1624	7.456	0.02189
0.4108	17.96	0.02183

At the conclusion of this series of experiments, the plug of glass wool was removed and placed in a platinum dish with some freshly boiled water; no alkaline reaction was detected by phenolphthalein.

A specimen of glass wool, as received from the dealers, on similar treatment reacted alkaline. 0.6772 Gram of this unwashed glass wool was boiled with 50 c.c. of water for three to five minutes and the solution titrated with *N* 50-acid. After neutralisation, it was again boiled and titrated. This procedure was continued until no alkaline reaction was shown on further boiling.* The alkali present was equivalent to 0.25 per cent. of NaOH calculated on the weight of the wool.

Another sample of glass wool was boiled under reflux with 100 c.c. of water for six hours. The alkali present was equivalent to 0.63 per cent. of NaOH.

Glass wool which had been boiled with water, dried at 110°, and left in a desiccator over-night, was placed in the vapour-pressure apparatus and air, saturated with moisture, passed over it until the weight of water vapour per litre of saturated air showed that the glass wool had retained a maximum quantity of water vapour. The water in the saturator was now replaced by a solution of 43.75 (weight) per cent. sulphuric acid having a vapour pressure of 11.56 mm. of mercury at 25° (Landolt, Börnstein, and Meyerhoffer, *op. cit.*, p. 426). Air was aspirated through this acid, and its vapour pressure determined.

Gram of water collected (<i>w</i>).	Volume (litres) of moist air aspirated at 760 mm. and 25° (<i>V</i>).	Vapour pressure of H ₂ SO ₄ solution (<i>f'</i>).
0.0380	3.356	12.0
0.0722	6.349	11.64
0.0454	4.043	11.69
0.0436	3.890	11.67
0.0330	2.990	11.50

$$f' = \frac{w}{V} \times \frac{298}{273} \times \frac{760}{0.7962} \text{ mm. of Hg.}$$

(0.7962 Gram is the weight of 1 litre of aqueous vapour at 760 mm. and 0°.)

The gradual fall of vapour pressure indicates that glass wool can lose some of its adsorbed water until the amount of the latter is in agreement with the partial pressure of aqueous vapour in the air, aspirated over it.

The measurement of the dissociation pressures of the salts was now commenced by a method similar to that used by Partington. No glass wool plug was used, and the absorption tubes contained pumice which had been boiled with sulphuric acid, and phosphoric oxide (Fig. 1, *loc. cit.*). These absorbents were renewed when a U-tube showed an increase in weight of 0.2 gram.

If w_1 and w_2 = grams of water vapour absorbed from the salt and from the water, respectively; V = litres of dry air aspirated at t° ; p = the dissociation pressure of the salt at t° ; π = the vapour pressure of the water at t° ; B = barometric height; and b = difference of the levels in the gauge fitted to the large regulating bottle, connected with a water-pump, then the weight of water vapour

in $V \left(\frac{B}{B-p} \right)$ litres of moist air in equilibrium with the salt will be

$$V \left(\frac{B}{B-p} \right) \left(\frac{p}{760} \times \frac{273}{273+t} \right) 0.7962 = w_1 \text{ grams.}$$

The weight of water in $V\left(\frac{B-b}{B-b-\pi}\right)$ litres of moist air in equilibrium with the water will be

$$V\left(\frac{B-b}{B-b-\pi}\right)\left(\frac{\pi}{760} \times \frac{273}{273+t}\right) 0.7962 = w_2 \text{ grams.}$$

Therefore
$$\frac{w_1}{w_2} = p/\pi \left(\frac{B}{B-p}\right)\left(\frac{B-b-\pi}{B-b}\right)$$

and
$$p = \frac{w_1}{w_2} \pi \left(\frac{B-p}{B}\right)\left(\frac{B-b-\pi}{B-b}\right)$$

If
$$p' = \frac{w_1}{w_2} \pi \quad \text{and} \quad K = \frac{B-b-\pi}{B-b},$$

then
$$p = \frac{p'KB}{B + p'KB}.$$

Unfortunately, the necessity of measuring this difference of pressure (b mm. of Hg) between the air in the large bottle and the atmosphere was not realised until the experiments at 25° had been carried out. It has been found from the later experiments that b has a constant value of 30 mm. of mercury.

Substitution of values of $(B-b)$ from 710 mm. to 750 mm. in the last expression, however, shows no difference in the calculated value of p from p' at 25° .

The use of this formula in place of the expression, $p = w_1\pi/w_2$, used by Partington, eliminates the correction for the change of pressure due to the height of the water in the saturator and also the error pointed out by Berkeley.

About fifteen minutes before each experiment was finished, the ground-glass joints connecting the absorption **U**-tubes were gently warmed with a hot tile until all the moisture was driven into the **U**-tube. The tube was allowed to cool (about five minutes were required) and the air current was then discontinued.

For measurements at higher temperatures, the end of the large **U**-tube, containing the salt, was hermetically sealed and the tube was completely immersed under water. To this arm, an absorption apparatus exactly like that used with the water-bubbler, was fused.

Copper Sulphate Pentahydrate, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$.

Each limb of the **U**-tube was packed with a column, 12–15 cm. long, of finely powdered copper sulphate (A.R. standard), which had been allowed to dry in the air for a week, and air was aspirated over it for six hours. As the first measurements were low, the contents of one limb of the **U**-tube were removed and well mixed with

copper sulphate which had been kept in a desiccator over sulphuric acid. This column was then replaced and the measurements were recommenced. At the conclusion of the experiments, it was found that the salt had effloresced, to a depth of 1 inch, near the air inlet, and this part was separated sharply from the rest, which was apparently unchanged.

Temperature 25°.		$\pi_{25^\circ} = 23.76$ mm.	$b = 30$ mm.	
w_1 .	w_2 .	p' mm.	B .	p mm.
0.0638	0.3528	4.30		
0.0412	0.2054	4.77		
0.0420	0.4626	2.16*		
0.0186	0.1147	3.68		
0.0090	0.0316	6.77		
0.0198	0.0904	5.20		
0.0078	0.0264	7.02		
0.0100	0.0306	7.76	774.5	7.94
0.0106	0.0328	7.68	766.0	7.86
0.0058	0.0180	7.65	762.5	7.83
0.0118	0.0360	7.70	762.5	7.88
0.0128	0.0394	7.72	761.0	7.90
0.0114	0.0345	7.85	765.6	8.03
0.0108	0.0328	7.82	771.4	8.00

Mean values: $p' = 7.73$, $p_{25^\circ} = 7.92 \pm 0.03$ mm.

Temperature 30°.		$\pi_{30^\circ} = 31.83$ mm.	$b = 30$ mm.	
w_1 .	w_2 .	p' mm.	B .	p mm.
0.01215	0.03416	11.33	762.5	11.68
0.01258	0.03487	11.43	758.4	11.78
0.01179	0.03259	11.45	755.4	11.80
0.01032	0.02918	11.26	758.0	11.52
0.01024	0.02833	11.51	775.0	11.85
0.01309	0.03625	11.48	776.5	11.82

Mean values: $p' = 11.41$, $p_{30^\circ} = 11.74 \pm 0.05$ mm.

Temperature 35°.		$\pi_{35^\circ} = 42.19$ mm.	$b = 30$ mm.	
w_1 .	w_2 .	p' mm.	B .	p mm.
0.01495	0.03849	16.39	765.5	17.00
0.01291	0.03283	16.59	760.7	17.21
0.01213	0.03159	16.20	760.8	16.81
0.01054	0.02714	16.39	761.3	17.00
0.01045	0.02670	16.51	758.0	17.13
0.01016	0.02604	16.45	768.5	17.06
0.01051	0.02752	16.12	758.1	16.73
0.01462	0.03735	16.51	768.3	17.13

Mean values: $p' = 16.39$, $p_{35^\circ} = 17.01 \pm 0.06$ mm.

* After mixing with copper sulphate which had been kept for five days in a desiccator.

Except those at 25°, the low results obtained during the initial induction period have been omitted.

Sodium Arsenate Dodecahydrate, $\text{Na}_2\text{HAsO}_4 \cdot 12\text{H}_2\text{O}$.

The U-tube was packed with freshly recrystallised, air-dried sodium arsenate, and air was aspirated over the salt for six hours before measurements were taken. The values during the induction period are omitted.

Temperature 25°.		$\pi_{25} = 23.76$ mm.		$b = 30$ mm.
w_1	w_2	p' mm.	B	p mm.
0.01008	0.02183	10.96	761.7	11.18
0.01844	0.04050	10.81	762.6	11.03
0.01131	0.02472	10.86	766.1	11.08
0.01626	0.03542	10.91	753.7	11.11
0.01075	0.02345	10.89	757.7	11.19
0.01211	0.02656	10.83	759.1	11.04

Mean values : $p' = 10.88$, $p_{25} = 11.10 \pm 0.03$ mm.

Temperature 30°.		$\pi_{30} = 31.83$ mm.		$b = 30$ mm.
w_1	w_2	p' mm.	B	p mm.
0.02435	0.05200	14.88	761.4	15.24
0.01876	0.03974	15.03	758.4	15.40
0.01773	0.03773	14.87	755.4	15.24
0.01870	0.03984	14.95	758.0	15.32
0.02563	0.05536	14.74	775.0	15.11
0.01600	0.03436	14.82	776.5	15.19

Mean values : $p' = 14.88$, $p_{30} = 15.25 \pm 0.04$ mm.

Temperature 35°.		$\pi_{35} = 42.19$ mm.		$b = 30$ mm.
w_1	w_2	p' mm.	B	p mm.
0.01138	0.02390	20.09	760.7	20.73
0.02131	0.04470	20.10	761.3	20.74
0.01005	0.02126	19.95	754.0	20.59
0.01206	0.02526	20.14	758.0	20.79
0.01196	0.02516	20.05	760.8	20.69
0.01032	0.02161	20.15	768.3	20.80
0.01002	0.02091	20.22	768.5	20.86

Mean values : $p' = 20.10$, $p_{35} = 20.74 \pm 0.03$ mm.

Results.

$\text{CuSO}_4 \cdot 5\text{H}_2\text{O} \longrightarrow \text{CuSO}_4 \cdot 3\text{H}_2\text{O}$		Method.	25°.	30°.	35°.
Frowein	Tensimeter		7.34 mm.	10.10 mm.	15.60 mm.
Partington	Transpiration		7.75 "		
			(at 25.01°)		
Menzies	Tensimeter		7.74 "		
"	Transpiration		7.80 "		
Wilson	Static		7.80 "		
This research	Transpiration		7.92 "	11.74 "	17.01 "

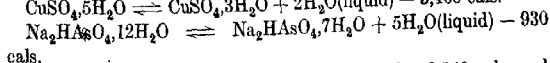
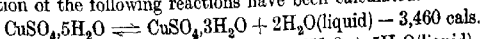
Partington's value has been recalculated, using $\pi_{25.01} = 23.77$ mm. in place of 23.56 mm. and is comparable with the value $p'_{25} = 7.73$ (see page 168).

$\text{Na}_2\text{HAsO}_4 \cdot 12\text{H}_2\text{O} \longrightarrow \text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$		25°.	30°.	35°.
Lescœur (<i>Ann. Chim. Phys.</i> , 1890, 21 , 511)		9.8 mm.	15.0 mm.	
This research		11.10 "	15.25 "	20.74 mm.

The limits of error in the results obtained by various investigators are tabulated below.

Partington	0.1 mm.
Baxter and Lansing	0.02 mm.
Wilson	0.01—0.1 mm.
Noyes and Westbrook	0.1—2.0 mm.
This research	0.03—0.06 mm.

By means of the van't Hoff reaction isochore the heats of hydration of the following reactions have been calculated.



For copper sulphate, Frowein obtained the value 3,340 cal. and Thomsen 3,410 cal. by direct calorimetric measurement.

It seems probable that the glass wool used in Partington's experiments became saturated with moisture before the induction period, when low pressures are obtained, was completed, and by then further retention of water vapour by the glass wool had ceased. Consequently the presence of glass wool would not vitiate Partington's results, but it is suggested that the larger limits of error in his experiments may be due to slightly irregular evaporation and condensation of moisture on the glass wool.

Summary.

The dissociation pressures of some hydrated salts have been measured at several temperatures by a dynamical method without the use of glass wool plugs.

The following values have been obtained.

Temp.	25°.	30°.	35°.
$\text{CuSO}_4 \cdot 5\text{H}_2\text{O} \rightarrow \text{CuSO}_4 \cdot 3\text{H}_2\text{O} \dots$	7.92 mm.	11.74 mm.	17.01 mm. of Hg.
$\text{Na}_2\text{HAsO}_4 \cdot 12\text{H}_2\text{O} \rightarrow$			
$\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O} \dots \dots \dots$	11.10 "	15.25 "	20.74 " "

The heats of hydration calculated from these results are 3,460 and 930 gram-cals., respectively.

In conclusion, we desire to thank the Chemical Society for a grant which has defrayed the expenses incurred in connexion with this work.

THE CHEMICAL DEPARTMENT,
EAST LONDON COLLEGE,
UNIVERSITY OF LONDON.

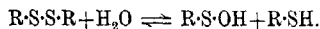
[Received, December 8th, 1922.]

XXI.—Production and Reactions of 2-Dithiobenzoyl.

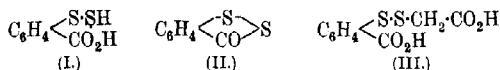
By MARY MCKIBBEN and ERNEST WILSON MCCLELLAND.

DITHIOBENZOYL has previously been prepared (T., 1922, **121**, 86) by the action of hydrogen sulphide on 2-thiolbenzoic acid in presence of concentrated sulphuric acid. The formation of this compound finds a ready explanation on the hypothesis advanced by Smiles

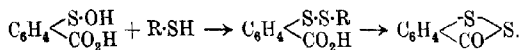
(T., 1911, 99, 640) that the aromatic disulphides and mercaptans react in sulphuric acid in accordance with the equation



The addition of hydrogen sulphide to such an equilibrium mixture in all probability gives rise, in the case of 2-thiolbenzoic acid, to a compound of the type I, which by intramolecular condensation yields 2-dithiobenzoyl (II).



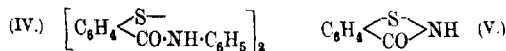
It has also been shown that thioglycollic acid may be substituted for hydrogen sulphide; in this case the formation of the intermediate compound III, which was isolated, suggests that 2-thiolbenzoic acid reacts with aliphatic substances containing the thiol group in accordance with the scheme



The possibility of synthesising 2-dithiobenzoyl by the interaction of 2-thiolbenzoic acid with aliphatic mercaptans has now been investigated. The particular substances examined were ethyl mercaptan and thiolacetic acid, both of which have been found to react with 2-thiolbenzoic acid in presence of sulphuric acid to give 2-dithiobenzoyl. In the case of ethyl mercaptan it was found necessary to use a higher temperature than that usually required, which may be accounted for by the relative stability of the thiol group in ethyl mercaptan.

From these results and those previously obtained, it is evident that the formation of 2-dithiobenzoyl by the interaction of aliphatic mercaptans and 2-thiolbenzoic acid in presence of sulphuric acid is of a general nature.

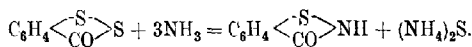
In a previous communication (*loc. cit.*) it has been shown that 2-dithiobenzoyl reacts with aniline, yielding the diamide of dithiobenzoic acid (IV), the reaction being accompanied by evolution of hydrogen sulphide. Sodium ethoxide has also been shown to react in an analogous manner, yielding dithiobenzoic acid by rupture of the dithio-ring and removal of sulphur.



The instability of the dithio-ring in presence of basic substances is thus apparent. The action of several bases on 2-dithiobenzoyl has been examined in order to determine how far the basic nature

of a compound influences the rupture of the dithio-system. Dimethylaniline, pyridine, and quinoline have yielded negative results, from which it would appear that basic character alone is not sufficient to effect removal of sulphur. The fact that hydrogen sulphide is continuously evolved in the reaction with aniline suggests that the sulphur of the dithio-ring is removed as hydrogen sulphide, a change which is not likely to occur in the cases cited above owing to the absence of replaceable hydrogen.

With ammonia, such a removal of sulphur should be possible. On treating an alcoholic solution of 2-dithiobenzoyl with dry ammonia, a compound was isolated which from its properties appears to have the structure represented by V. The formation of such a substance, the imide of 2-thiolbenzoic acid, can readily be explained on the above assumption, the hydrogen sulphide evolved being converted to ammonium sulphide thus :



On oxidation with potassium permanganate, 2-thiobenzimide yields "saccharin."

EXPERIMENTAL.

2-Dithiobenzoyl (Formula II).

(a) *From Thiolbenzoic Acid and Ethyl Mercaptan*.—A solution of 1 gram of ethyl mercaptan in 5 c.c. of concentrated sulphuric acid was mixed with a solution of 1 gram of 2-thiolbenzoic acid in 10 c.c. of concentrated sulphuric acid. After keeping for a short time, the mixture was heated at 50° for two and a half hours with frequent shaking. The solution was then poured on to crushed ice, and the 2-dithiobenzoyl removed by volatilisation in a current of steam and purified by crystallisation from alcohol. The substance was found to be identical with 2-dithiobenzoyl from other sources.

(b) *From 2-Thiolbenzoic Acid and Thiolacetic Acid*.—To a solution of 5 grams of 2-thiolbenzoic acid in 50 c.c. of concentrated sulphuric acid, 5 grams of thiolacetic acid were gradually added, and the mixture was heated at 50° for two hours. The solid precipitated on pouring the mixture into ice-water was removed in a current of steam and crystallised from alcohol. The resulting compound was found to be 2-dithiobenzoyl by comparison with material prepared by other methods.

Reaction of Ammonia with 2-Dithiobenzoyl.

Dry ammonia was passed into an alcoholic solution of 2-dithiobenzoyl for two hours, the alcoholic solution was then partly

evaporated, and the dissolved material precipitated by addition of water. The crude substance thus obtained was gently heated with a small quantity of 50 per cent. sodium hydroxide, any undissolved material being filtered off. On cooling, the sodium salt of 2-thiobenzimide crystallised in fine, transparent needles, which were collected and washed with sodium hydroxide solution. The sodium salt was then dissolved in water, and the imide precipitated by the addition of hydrochloric acid. 2-Thiobenzimide (formula V) crystallises from aqueous alcohol in long, white, needle-shaped crystals; it melts at 158° , dissolves in hot water, and is readily soluble in most organic media. With alcoholic ferric chloride, it gives a purple coloration; on addition of water, the solution deposits a blue powder and the original imide (Found: C = 55.9; H = 3.5; S = 21.1; N = 9.3. C_7H_5ONS requires C = 55.6; H = 3.3; S = 21.2; N = 9.3 per cent.).

Oxidation of 2-Thiobenzimide.

2-Thiobenzimide was heated with an excess of aqueous potassium permanganate for several hours. Alcohol was then added, and the precipitated manganese dioxide filtered off and well washed with hot water. The filtrate and washings after concentration were acidified with hydrochloric acid, which precipitated a white, crystalline solid. This substance melts with decomposition at about 227° , possesses an intensely sweet taste, and answers to tests for o-benzoic sulphinide ("saccharin").

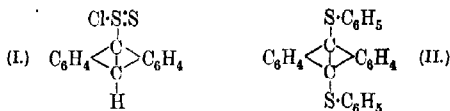
THE SIR DONALD CURRIE LABORATORIES,
QUEEN'S UNIVERSITY, BELFAST. [Received, November 30th, 1922.]

XXII.—*The Investigation of meso-Thioanthracene Derivatives. Part I. Observations on the Production of Dithioanthraquinone, Dithiodianthrone, and other Closely Related Derivatives.*

By ISIDOR MORRIS HEILBRON and JOHN STANLEY HEATON.

It is somewhat remarkable that, although 1- and 2-thiolanthraquinones and various anthraquinone sulphides have been prepared (compare Gattermann, *Annalen*, 1913, **393**, 113; Schaarschmidt, *ibid.*, 1915, **409**, 59), as also thiolanthracene (Hefter, *Ber.*, 1895, **28**, 2258), only very few meso-thioanthracene derivatives have hitherto been described. By the action of sulphur chloride on

anthracene dissolved in light petroleum, Lippmann and Pollok* (*Ber.*, 1901, **34**, 2768) obtained a compound melting at 212° to which they ascribe the constitution shown in formula I. Bistrzycki and Brenken (*Helv. Chim. Acta*, 1922, **5**, 20) also have recently



prepared 9-phenyl-9:10-dihydro-*meso*-thioanthracene, in which the sulphur is apparently present as a bridge atom, by the action of concentrated sulphuric acid on 2:4:4-triphenyl-1:3-oxthiophan-5-one.

The present investigation was undertaken with the object of examining the methods of formation of *meso*-thioanthracene derivatives, and gives the results of certain experiments which have resulted in establishing the existence of a series of thio-derivatives, some of which are quite analogous to the known oxygen compounds.

As both 1- and 2-thiolanthraquinones have been obtained by heating the corresponding chloro-derivatives with sodium sulphide, we attempted, in the first instance, to prepare *meso*-dithiolanthracene by a similar method, starting from either 9:10-dichloro- or -dibromo-anthracene. Although many experiments were carried out, employing both anhydrous sodium sulphide, as also sodium hydrosulphide, in no case was more than the merest trace of any sulphur-containing compound obtained. That, however, the halogen atoms in the 9:10-position can be replaced by sulphur was exemplified by the preparation of *dithioanthraquinyl diphenyl ether* (II) by the interaction of phenyl mercaptan and 9:10-dibromoanthracene in benzene solution in presence of piperidine under pressure at a temperature of 200°.

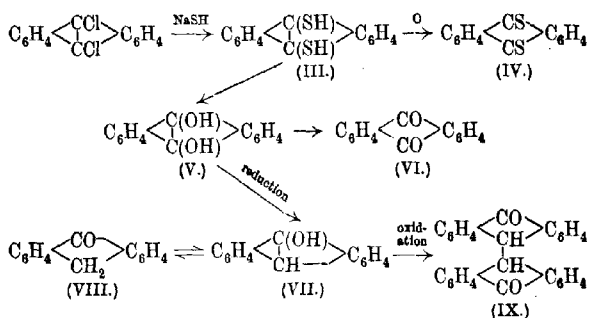
As a result of this experiment, it seemed likely that the mercaptan group might be introduced into the anthracene molecule by having the reactants in solution, and the next method adopted by us was one similar to that employed by Vorländer and Mittag (*Ber.*, 1913,

* Since this communication was submitted, a paper by Friedländer and Simon has appeared (*Ber.*, 1922, **55**, [B], 3969) in which these authors find that, by the direct action of sulphur chloride on anthracene, anthranyl-9-dithiochloride, $\text{C}_{14}\text{H}_9\text{S}\cdot\text{SCl}$, is obtained in 90 per cent. yield. This compound, which melts at 117–118°, on treatment with sodium sulphide yields the sodium salt of 9-anthranyl mercaptan (thioanthranol), from which the free mercaptan is obtained as an orange-yellow precipitate on acidification with dilute acetic acid. The mercaptan is very readily oxidised, yielding dianthranyl disulphide.

46, 3453), who obtained the highly labile triphenylcarbinyl mercaptan by saturating a solution of sodium ethoxide in ethyl alcohol with hydrogen sulphide and heating the resulting solution of sodium hydrosulphide with *o*-chlorotriphenylmethane. We hoped in this way, starting from 9:10-dichloroanthracene, to be able to obtain the free 9:10-dithiolanthracene (III) which, on oxidation, would yield dithioanthraquinone (IV) by a reaction similar to the ready oxidation of anthraquinol (V) to anthraquinone (VI). Working under the conditions specified by Vorländer and Mittag, no reaction whatsoever could be induced, but, after heating under pressure at a temperature of 120°, sodium haloid was formed, indicating that interaction had been brought about. A mass of mixed crystals was also found to have been deposited on the sides of the autoclave, which were separated by fractional crystallisation from benzene, yielding unchanged dichloroanthracene and anthraquinone.

On working up the alcoholic solution, there was obtained, as explained in detail in the experimental part, a pale yellow powder which, just after precipitation, is completely soluble in hot aqueous sodium hydroxide, and proved to consist mainly of a mixture of anthranol and anthrone (compare K. Meyer, *Annalen*, 1910, **379**, 37). If, however, the crude product is first dried, it is no longer wholly soluble in aqueous alkali and, in addition to anthranol and anthrone, dianthrone is now present. The last compound must consequently have appeared subsequently to the reaction in the autoclave and is doubtless formed by oxidation of the anthranol by atmospheric oxygen, similarly to the production of 3:3'-dihydroxydianthrone from 2-hydroxyanthranol (A. G. Perkin, T., 1922, **121**, 289). This explanation meets with additional support from the work of K. Meyer (*loc. cit.*), who has shown that, in the case of anthrone, oxidation is subsequent to enolisation to anthranol, although the product is always the ketonic dianthrone. In attempting to account for the formation of these substances, we consider that the first reaction which takes place is the formation of *meso*-dithiolanthracene, and in support of this assumption is the fact that, in addition to the anthrone derivatives, a small quantity of a sulphur-containing substance has invariably been isolated. This substance, which melts unsharply at 207°, has also been obtained directly from dithioanthraquinone (p. 183), and it may thus be reasonably concluded that its presence in this reaction undoubtedly points to the primary formation of the mercaptan. It is further assumed that, in presence of the large excess of ethyl alcohol, or possibly owing to traces of water present, the labile dimercaptan is converted into anthraquinol, such action being favoured by the high

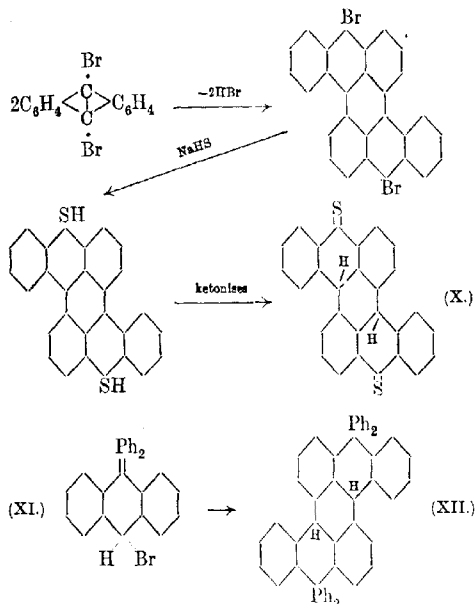
pressure and elevated temperature. At this stage, the reducing properties of the sodium hydrosulphide come into play and anthranol (VII) is formed, which tautomerises in solution to anthrone (VIII) until equilibrium is reached. At this point there are present anthraquinol, anthranol, and anthrone. When the autoclave is opened, the anthraquinol oxidises to anthraquinone, and the anthranol partly changes to dianthrone (IX).



From the results obtained in this experiment, it is evident, not only that interaction between 9:10-dichloroanthracene and sodium hydrosulphide can be induced, but also that, in all probability, 9:10-dithiolanthracene is the primary product formed. It appeared probable, moreover, that if the use of ethyl alcohol was avoided, the secondary formation of oxygen compounds might be altogether excluded, and we accordingly decided to employ amyl alcohol in its place, and also to avoid the use of the autoclave, with the idea of thus minimising the risk of bringing about coalescence of the anthracene molecules. The exact quantity of sodium^{*} was accordingly dissolved in amyl alcohol, and the solution saturated with dry hydrogen sulphide. 9:10-Dibromoanthracene^{*} was then added and the stream of gas continued first in the cold and then in the heat, until no dibromoanthracene separated out on cooling, the constant stream of hydrogen sulphide being maintained throughout. In every experiment carried out under these conditions, a bright yellow substance is gradually thrown out of solution, which, after crystallisation from nitrobenzene, gives an analysis in agreement with that required for *dithioheptacyclene* (X). This has apparently resulted from a fusion of two anthracene molecules with loss of hydrogen bromide, as indicated below, a

^{*} Experience has shown that this reacts better than the analogous dichloro-derivative.

reaction analogous to the production by Liebermann and Lindenbaum (*Ber.*, 1905, **38**, 1799) of tetraphenylheptacyclic (XII) from 10-bromo-9:9-diphenyldihydroanthracene (XI).



On directing our attention to the working up of the cold amyl alcohol solution, we have found that, despite every precaution to maintain apparently identical conditions in each experiment, the products obtained vary very considerably in composition. Although at first sight this may appear strange, a little consideration will show that, providing 9:10-dithiolanthracene is the initial reaction product, then, as illustrated in Table I, this substance can undoubtedly react further to produce more complex condensation products in which the determining factor for any one special reaction would, in all probability, depend on very minute alterations in the conditions, exceedingly difficult, if not altogether beyond ordinary methods of control. That this is so is shown in the following, where a few typical examples out of a great number of experiments actually carried out, are recorded. In our first experiment, the cold amyl alcohol solution, on standing, deposited a few grams of a substance which, on recrystallisation from benzene, was

obtained in reddish-brown crystals melting at 176° . This compound, which is exceedingly labile and soon decomposes on standing in air, appears from analysis to be dithioanthraquinone. Unfortunately, we have failed up to the present to obtain this substance again, and consequently, apart from the fact of having ascertained that it readily yields anthraquinone on treatment with dilute nitric acid, we have been unable to examine its properties in closer detail. After leaving it to stand for a fortnight in air, on then recrystallising the residue from acetone, a substance melting at about 207° was obtained, which produced no depression in melting point when mixed with the sulphur compound obtained in the ethyl alcohol experiment. Analysis of this substance gave no definite indication as to its structure, and the quantities at our disposal were too small for further investigation.

On repeating the previous experiment, the filtered amyl alcohol solution, after removal of dithioheptacyclene, deposited a mixture of red and yellow crystals, which were separated by fractional crystallisation from benzene, in which the red crystals were more readily soluble. The main fraction consisted of bright yellow crystals, melting at 194° , and has the composition of *bisthioanthrone disulphide* (XIII).

On concentration of the amyl alcohol mother-liquors, a dark red, crystalline compound was obtained which, after recrystallisation from benzene, melted at 202° , and was identical with the red crystals separated from (XII). That this substance is *dithio-dianthrone* (XIV) is conclusively proved by the fact that, on treating it with yellow mercuric oxide, dianthrone results. In the experiment in which the dithioanthraquinone was obtained, the filtered amyl alcohol solution remained bright red throughout, but in the majority of our experiments wherein *bisthioanthrone disulphide* was isolated in quantity, although the solution was bright red when hot, the cold solution invariably changed to yellow. We have found, however, that even these colour changes do not necessarily occur, and in one particular experiment the solution merely became darker as the reaction proceeded, and deposited a smaller quantity than usual of (X). In this case, the clear amyl alcohol solution on cooling deposited a light brown powder, which was separated by benzene into a small quantity of unchanged dibromoanthracene together with a substance of composition $C_{22}H_{18}S_3$, probably *bisthioanthrone sulphide* (XV).

It seems likely, in view of the fact that in this experiment some 9:10-dibromoanthracene was recovered, that, the different course of the reaction was due to the fact that an insufficiency of sodium had inadvertently been employed, and it is our intention to pursue

these investigations further, with very careful control of the sodium content.

Finally, it remains to be recorded that in one other experiment, where the reaction had yielded both substances (X) and (XIII), we found, on concentration of the mother-liquors, that, in place of the anticipated dithiodianthrone, a substance was obtained which, after recrystallisation from xylene, separated in small, faintly red prisms melting at 174—176°. This substance, however, is entirely different from dithioanthraquinone and the results of its analysis agree well with the composition of *dianthranyl sulphide* (XVI). In agreement with such a structure, we have isolated anthracene (in the form of its picrate) as one of the products after reduction of the compound with zinc and acetic acid.

EXPERIMENTAL.

meso-Dithioanthraquinyl Diphenyl Ether (Formula II).—Twenty grams of 9:10-dibromoanthracene were dissolved in 1 litre of benzene and mixed with 25 grams of phenyl mercaptan together with 40 grams of piperidine. After heating for six hours at 180° under pressure, the reaction mixture was filtered from piperidine hydrobromide, the solvent distilled off, and the crude product purified by recrystallisation from chloroform. *Dithioanthraquinyl diphenyl ether* forms bright yellow needles melting at 212°. It is exceedingly stable and is not hydrolysed on heating either with alkali or with concentrated hydrochloric acid. On warming with fuming nitric acid, it breaks down, yielding anthraquinone (Found: C = 78·8; H = 4·9. $C_{26}H_{18}S_2$ requires C = 79·2; H = 4·6 per cent.).

Treatment of 9:10-Dichloroanthracene with Sodium Hydrosulphide in Ethyl Alcohol Solution.—Forty grams of sodium were dissolved in 800 c.c. of absolute alcohol and the solution completely saturated with dry hydrogen sulphide. Ninety grams of finely powdered 9:10-dichloroanthracene were then added and the stream of hydrogen sulphide continued for a further half-hour, after which the reaction mixture was transferred to an autoclave and heated for two hours at 120°. On opening the autoclave after cooling, a mass of crystals was found deposited on the sides of the vessel. These were filtered off, and thoroughly washed with hot water to remove sodium salts. On recrystallisation of the dried product from benzene, 40 grams of unchanged dichloroanthracene were recovered, whilst from the mother-liquors there were obtained a few grams of a sulphur-free substance which melted at 280° and was identified by the oxanthranol test as anthraquinone.

The clear alcoholic solution, on standing, deposited a small

quantity of a crystalline sodium salt which was readily hydrolysed by boiling water, yielding a fine yellow powder, a further quantity of which was obtained on dilution of the alcoholic mother-liquors (total solids = 30 per cent. of halogen compound employed). A portion of the freshly precipitated substance, while still in the moist state, was immediately recrystallised from glacial acetic acid, when pale yellow needles melting at 120° (rapid heating) were obtained. The fresh crystals were completely soluble in cold dilute alkali, but when left to dry on a porous plate, were partly changed to an alkali-insoluble compound, showing an indefinite melting point. The alkali-soluble compound was found to be free from sulphur and corresponded in all respects with anthranol (K. Meyer, *loc. cit.*).

The remainder of the crude product was allowed to dry and taken up in hot methyl alcohol, in which the bulk was readily soluble, a small, insoluble residue being retained. By the successive addition of small quantities of water to this solution, three fractions were obtained:

(a) A brown solid which melted at 170 – 185° and was not completely soluble in dilute alkali, even on boiling.

(b) A similar substance melting at 165° , somewhat more soluble in alkali than fraction (a).

(c) A substance melting between 130 – 160° which was completely soluble in hot aqueous alkali.

Fraction (a).—The alkali-soluble portion of this fraction was removed by repeated extraction with hot dilute sodium hydroxide solution. The insoluble portion was then recrystallised from absolute alcohol, when pale yellow crystals, melting with charring at 240° , were obtained. These were soluble in hot alcoholic potash and identified as dianthrone by the melting point of its mixture with dianthrone, prepared according to the method of K. Meyer (*loc. cit.*). That no anthraquinone was present was shown by the fact that no colour reaction was given on reduction with zinc dust and sodium hydroxide solution.

Fraction (c).—By careful fractional crystallisation of this fraction from absolute alcohol, a substance melting between 165° and 168° was obtained, which was free from sulphur and completely soluble in boiling aqueous sodium hydroxide. That it was actually anthrone was proved by treatment with bromine in carbon disulphide solution, when yellow crystals of bromoanthrone, melting at 148° , were obtained.

The residue, insoluble in methyl alcohol, yielded on recrystallisation from chloroform a minute quantity of a yellow, crystalline substance melting at about 207° . This substance contained

sulphur, but the quantity at our disposal was too small to permit of any further examination being made.

Treatment of 9:10-Dibromoanthracene with Sodium Hydrosulphide in Amyl Alcohol Solution.—5.5 Grams of sodium were dissolved in $1\frac{1}{2}$ litres of pure amyl alcohol, contained in a round-bottom flask fitted with a reflux condenser and calcium chloride drying tube. The sodium amyloxide solution was then saturated with dry hydrogen sulphide, which was led in through an inverted thistle funnel, 40 grams of 9:10-dibromoanthracene were added, and the stream of gas was maintained for a further half-hour in the cold, after which the solution was boiled under reflux until no dibromoanthracene separated on cooling. The reaction was complete after about twelve hours' heating, during the whole of which period hydrogen sulphide was passed into the solution. The course of the reaction can generally be followed owing to the fact that the colour of the solution changes from yellow to bright red towards the end of the reaction.

Dithioheptacyclene (Formula X).—This substance, which was gradually thrown out of solution as the reaction proceeded, was collected and purified by boiling first with water and then with glacial acetic acid to remove the last traces of sodium salts. The dried compound was next boiled with benzene, in which it is insoluble but which removes small quantities of soluble organic compounds. After crystallisation from nitrobenzene, it was obtained in small, yellow crystals, melting at 320° and insoluble in the usual organic solvents (yield of pure substance: 4 grams) (Found: C = 80.8; H = 3.9; S = 15.2. $C_{28}H_{16}S_2$ requires C = 80.8; H = 3.8; S = 15.4 per cent.).

Dithioanthraquinone.—In the first experiment carried out, it was found that, on standing, the cold amyl alcohol solution deposited red crystals, which were filtered off and dried. After repeated fractional crystallisation from benzene, a separation of the crude substance into two portions was effected: (a) a small quantity of a brick-red substance melting between 190 — 198° , (b) 5 grams of a red, crystalline substance melting at 170 — 174° . The latter fraction was again recrystallised from benzene, when small, ruby-red crystals separated out, melting sharply at 176° (Found: S = 26.2. $C_{14}H_8S_2$ requires S = 26.6 per cent.). This substance, which we consider to be pure *dithioanthraquinone*, is readily soluble in benzene or chloroform, but only slightly soluble in alcohol, acetone, or ethyl acetate. On oxidation with dilute nitric acid, it passes into anthraquinone, thus proving that the sulphur atoms are attached to the *meso*-carbon atoms of the anthracene molecule. On standing in air, dithioanthraquinone rapidly decomposes,

sulphur dioxide being evolved during the process. After leaving it to stand for a fortnight, a substance is obtained which gives no depression in melting point with the product isolated as fraction (a). The two fractions were consequently mixed and on recrystallisation from acetone yielded a compound melting unsharply at about 207°, which further proved to be identical with the sulphur compound previously obtained in the experiment using ethyl alcohol as solvent. An analysis of this failed to indicate any definite structure.

Owing to the fact that dithioanthraquinone gradually breaks down in air, we were unable to carry out a carbon and hydrogen estimation, and in order to do this and verify beyond doubt the correctness of the structure assigned, as also to examine this interesting compound in greater detail, a fresh preparation was started. Although apparently working under absolutely similar conditions in this and subsequent experiments, we have as yet failed again to isolate dithioanthraquinone except in very minute quantities.

Bisthioanthrone Disulphide (Formula XIII).—In the majority of our experiments, after removal of the dithioheptacyclic, the amyl alcohol solution deposited a mixture of red and yellow crystals. The mixed crystals were filtered off, and a separation effected by fractional crystallisation from benzene, when the following fractions were obtained: (a) yellow crystals melting at 192–194°, (b) an impure specimen of the same compound melting at 184–188°, (c) a very small quantity of a dark red solid (dithiodianthrone). After a final recrystallisation from chloroform, *bisthioanthrone disulphide* crystallised in very characteristic, bright golden-yellow needles (m. p. 194°) which are moderately soluble in benzene or chloroform but almost insoluble in alcohol or acetone. It is insoluble in aqueous alkali, but dissolves in alcoholic potash, and doubtless exists here as the potassium salt of the tautomeric dithiodianthranol derivative (Found: C = 69.5; H = 4.0; S = 26.1. $C_{28}H_{18}S_4$ requires C = 69.7; H = 3.7; S = 26.6 per cent.).

Dithiodianthrone (Formula XIV).—This substance is obtained on concentration of the amyl alcohol mother-liquors from which the *bisthioanthrone disulphide* has been removed. *Dithiodianthrone* crystallises from benzene in dark red prisms melting at 202°, readily soluble in chloroform or benzene, sparingly soluble in alcohol or ethyl acetate. Like *bisthioanthrone disulphide*, it is insoluble in aqueous alkali, but dissolves in alcoholic potash on warming. On oxidation with concentrated nitric acid, anthraquinone is obtained, whilst on heating in benzene solution with yellow mercuric oxide the sulphur atoms are replaced by oxygen

with formation of dianthrone (Found: C = 80.3; H = 4.6; S = 15.0. $C_{28}H_{18}S_2$ requires C = 80.4; H = 4.3; S = 15.3 per cent.).

Dianthranyl Sulphide (Formula XVI).—As shown in Table I, assuming the reduction of dithiolanthracene to thioanthranol to take place in the autoclave, the latter compound could obviously react further to yield either *dianthranyl sulphide* or dithiodianthrone. It is probable that in all experiments both compounds are actually formed in varying amounts, and the fact that their joint isolation has not been accomplished may be attributed to the experimental difficulties involved in separating neutral substances of very similar solubility. In several experiments, indeed, we altogether failed to obtain any definite compound from the cold amyl alcohol solution, brown mixtures being produced, which could not be separated by fractional crystallisation.

In one case, however, after removal of bisthioanthrone disulphide, on concentration of the amyl alcohol mother-liquors, in place of dithiodianthrone separating out, dianthranyl sulphide was obtained. This substance crystallises from xylene in bright red crystals melting at 174–176° (Found: C = 86.8; H = 4.9; S = 8.1. $C_{28}H_{18}S$ requires C = 87.1; H = 4.7; S = 8.3 per cent.).

That the constitution assigned is correct has been established in the following manner. One gram of dianthranyl sulphide was dissolved in boiling glacial acetic acid and, after the addition of excess of zinc dust, the whole heated under reflux for four hours. Hydrogen sulphide was evolved during the course of the reduction. After filtering off from excess of zinc, the reduction products were precipitated by water, and the residue taken up in dilute alkali, in which it was partly soluble. The insoluble portion was dissolved in alcohol and added to an alcoholic solution of picric acid, when the characteristic ruby-red anthracene picrate slowly crystallised out. $C_{28}H_{18}S + H_2 = C_{14}H_{10} + C_{14}H_9SH$.

Bisthioanthrone Sulphide (Formula XV).—Mention has already been made of the fact that, although in general the amyl alcohol solution changes from yellow to red as the reaction proceeds, we have found in certain experiments that the solution merely becomes darker and, in these cases, a smaller quantity of (X) is formed. In one of these experiments, the clear amyl alcohol solution, on cooling, deposited a light brown solid, which was separated by crystallisation from benzene into: (a) transparent, brown prisms melting at 218°, which, despite their abnormal appearance, proved to be unchanged 9:10-dibromoanthracene, (b) light brown crystals melting at 170–172°.

crystallisation from benzene into: (a) transparent, brown prisms

yellowish-brown crystals (m. p. 185°), moderately soluble in benzene or chloroform, sparingly soluble in alcohol, acetone, or ethyl acetate (Found: C = 74.6; H = 4.3; S = 21.4. $C_{25}H_{18}S_3$ requires C = 74.7; H = 4.0; S = 21.3 per cent.).

We desire to express our thanks to the Council of the Scientific and Industrial Research Department for a grant which has enabled this research to be carried out.

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[Received, November 29th, 1922.]

XXIII.—*Photocatalysis. Part III. The Photosynthesis of Naturally Occurring Nitrogen Compounds from Carbon Dioxide and Ammonia.*

By EDWARD CHARLES CYRIL BALY, ISIDOR MORRIS HEILBRON, and HAROLD JACOB STERN.

IN the previous communication (Baly, Heilbron, and Hudson, T., 1922, **121**, 1078), a brief account was given of the investigation of the products formed by the action of ultra-violet light on solutions of potassium nitrate saturated with carbon dioxide. It was shown that the nitrate and carbonic acid, respectively, are converted into nitrite and formaldehyde, which at once react to produce formhydroxamic acid. This acid then combines with more of the photo-synthesised formaldehyde to give a variety of products, amongst which were detected glyoxaline, two substances of alkaloidal nature, free α -amino-acids, and substituted α -amino-acids of the type of histidine. Brief mention was also made in that communication of the formation of methylamine and of pyridine by the action of the photochemically activated formaldehyde on ammonia, and it is proposed in the present paper to give an account of this branch of our work.

It might be argued that the photosynthesis of naturally occurring products by the action of the photochemically activated formaldehyde on ammonia has no direct bearing on the photosynthetic processes of the living plant, since ammonia in the free state does not exist in the plant and indeed is a poison to the plant. On the other hand, it is impossible to deny that ammonium nitrate may be present and that this may react with the formaldehyde to give formhydroxamic acid and ammonia. Then again, a knowledge of the products formed by the interaction of the formaldehyde and ammonia must necessarily be of service in interpreting the mechanism

of the photosynthesis of complex nitrogen compounds. No apology therefore is needed for emphasising the importance of the study of the reaction in question.

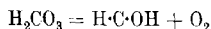
It may be noted at the outset that although the products of the action of light on carbonic acid and ammonia differ from those formed when carbonic acid and potassium nitrate are illuminated, the mechanism of the synthesis appears to be very similar in the two cases. In both cases it has been found that all the tests for reducing sugars give absolutely negative results and therefore it seems in the highest degree probable that the activated formaldehyde, as photosynthesised from the carbonic acid, combines in the one case with the nitrite to give formhydroxamic acid and in the other with the ammonia, and that the products of these two syntheses react with more of the activated formaldehyde to give complex nitrogen derivatives. The alternative suggestion that these complex nitrogen compounds are produced by interaction of the formhydroxamic acid or ammonia and active hexoses synthesised from the formaldehyde would seem to be disproved by the total absence of all reducing sugars from the solutions.

During the first part of the investigation aqueous solutions of ammonia, saturated with carbon dioxide, were exposed for various periods of time to the light from the quartz mercury lamp. The strength of the ammonia was in most cases 1.3*M* and the times of exposure varied from twenty to three hundred hours. The resulting solutions were evaporated under reduced pressure and the distillate was collected in aqueous hydrochloric acid. The acid distillate was evaporated to dryness at 100°, the dry hydrochloride extracted with absolute alcohol, and the filtrate evaporated to dryness. The residue was again extracted with absolute alcohol, this process being several times repeated. The final product was found in the main to be methylamine hydrochloride.

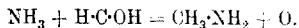
The residue in the distilling flask was found to contain nitric acid in the form of nitrate and it also reduced neutral and acid permanganate solutions, owing possibly to the nitrous acid which was also proved to be present, this doubtless having been formed photochemically from the nitric acid. The production of nitric acid along with the methylamine by the action of ultra-violet light on solutions of ammonia, saturated with carbon dioxide, was confirmed in a great number of experiments. In the first place, the ammonia solution employed was proved to contain no trace of either nitric or nitrous acid, and in the second place 1.3*M*-ammonia solution, saturated with carbon dioxide, gave no reaction for either acid after being kept in the dark for seventy hours at 40°, this being the maximum temperature to which the solutions were heated by the rays of the

mercury lamp. A similar solution after exposure to ultra-violet light for seventy hours gave very decided reactions for nitric acid. After three hundred hours, the reactions for this acid were very strong indeed, the solution giving a brilliant red colour with brucine and sulphuric acid, which faded to orange on standing. The orange colour changed to green on the addition of stannous chloride, this green colour disappearing on standing. The presence of some nitrous acid was also proved by the Griess-Illesvay test.

This formation of nitric acid is of some importance, since it must be produced by the oxidation of the ammonia by the nascent oxygen set free in the photosynthetic process. This photosynthesis must take place in two stages, first, the photosynthesis of formaldehyde by the action of light on the carbonic acid,



and, secondly, the interaction of the activated formaldehyde and the ammonia,



The oxidation of some of the ammonia to nitric acid is due to the oxygen that is set free in these two reactions. In the two previous papers (Baly, Heilbron, and Barker, T., 1921, 119, 1025; Baly, Heilbron, and Hudson, *loc. cit.*) the oxygen was proved to oxidise some of the formaldehyde to formic acid.

During the course of these early experiments the mixed hydrochlorides obtained in the manner already described were treated with sodium hydroxide and a very strong odour of pyridine was developed. It was at once realised that the photosynthetic process might lead to the formation of more complex compounds than methylamine, namely, compounds of the type of pyrrole, pyrrolidine, pyridine, and piperidine. This would not be surprising in view of the fact that Baudisch (*Ber.*, 1913, 46, 115) has shown that both pyrrole and pyridine derivatives are formed in solutions of potassium nitrite and methyl alcohol after long exposure to light. This was discussed in the previous paper, where it was stated that no evidence had then been found of the formation of any simple derivatives of pyrrole or pyridine when solutions of formhydroxamic acid and formaldehyde are exposed to ultra-violet light, these two substances being the first products of the photochemical synthesis from potassium nitrite and methyl alcohol. It was pointed out that under those conditions the photosynthesis is exceedingly rapid and very soon passes beyond the stage of simple compounds. The formation of pyridine in the present experiments by the action of light on solutions of ammonia saturated with carbon dioxide would therefore confirm Baudisch's observations. The synthesis

of the pyridine nucleus was investigated more fully as follows. Batteries of eight quartz tubes, each containing 100 c.c. of 1.3*M*-ammonia, saturated with carbon dioxide, were exposed to the light of the quartz mercury lamp for different periods. The solutions were concentrated under reduced pressure, the distillate being as before collected in hydrochloric acid. The concentrated solution left in the distilling flask was tested for hydroxylamine, hyponitrous acid, α -amino-acids, and sugars, but in every case these substances were absent. The absence of α -amino-acids is very significant in view of the readiness with which these substances are formed by the action of freshly photosynthesised formaldehyde on potassium nitrite.

The acid distillate was evaporated to dryness on the water-bath and the solid residue was dried in the desiccator. On extraction with absolute alcohol, a considerable quantity of methylamine hydrochloride was obtained which was identified by its melting point, the evolution of methylamine on treatment with alkali, and by the carbylamine test. The alcoholic extract was also found to contain small quantities of the hydrochloride of pyridine or, sometimes, the hydrochloride of piperidine. The presence of one or other of these compounds was recognised by the borax test. A small quantity of the mixed hydrochlorides is rubbed in a warm mortar with a little borax, when the smell of pyridine or piperidine is at once developed very strongly, the smell of methylamine not being noticeable for at least thirty seconds. This test, which was the standard method of testing for the presence of pyridine bases in ammonium salts employed during the war, is capable of detecting 0.03 per cent. of pyridine in ammonium chloride. It may be noted that, although in these experiments one of these bases is always formed, we have not as yet succeeded in determining the conditions for the photosynthesis of either one. In most cases pyridine was found, but in some experiments piperidine was apparently present.

The presence of pyridine (or piperidine) was confirmed in every case and it was proved by the most rigid tests that the original ammonia contained no trace of either base. The hydrochloride prepared by neutralisation of the ammonia gave no evidence of either pyridine or piperidine when treated with borax, nor was any evidence of these substances found when the ammonium carbonate solution had been heated for many hours at 40°. Furthermore, some of the ammonia was half neutralised with hydrochloric acid and the mixture concentrated in the distilling flask, the distillate being collected in acid. The concentration was continued until all the free ammonia had passed over, and if pyridine had been present the whole of it would now be found in the distillate. The

distillate was evaporated to dryness and extracted with absolute alcohol. The alcoholic extract contained no trace of pyridine bases. The solution of ammonium chloride left in the distilling flask was made alkaline with sodium hydroxide and heated, the ammonia being collected in pure water. The ammonia solution thus obtained was saturated with carbon dioxide and exposed to light, after which the presence of pyridine was at once detected. These results would seem to prove that piperidine or pyridine is always formed by the action on ammonia of formaldehyde as photosynthesised from carbonic acid by the action of ultra-violet light, and therefore it may be claimed that Baudisch's observations have been confirmed.

It is of some importance to note that we have succeeded in photocatalysing the synthesis of methylamine from ammonia and carbonic acid, and we also have obtained evidence of the photocatalytic synthesis of pyridine and piperidine. Under normal conditions, the synthesis only proceeds under the influence of ultra-violet light of very short wave-length, no reaction taking place if the ammonia-carbonic acid solutions are exposed in glass test tubes behind a plate-glass screen. If ammoniacal solutions of cupric carbonate, saturated with carbon dioxide, are thus exposed behind glass to the light from the mercury lamp, the photosynthesis takes place very rapidly. Methylamine is at once formed and after some hours' exposure strong evidence is obtained of the formation of pyridine or piperidine.

The copper solutions after exposure to light were treated in the same way as described above, the mixed bases being distilled into hydrochloric acid. The concentrated copper solution was filtered, the remaining copper precipitated as sulphide, and after being again filtered the colourless solution was evaporated to dryness. A small quantity of a white, deliquescent substance was obtained which was dissolved in ether to remove inorganic impurities. The ethereal solution on evaporation deposited white crystals resembling Prince of Wales's feathers. In three consecutive experiments the melting point was found to be 118° , 119° , and 122° , but we have not yet succeeded in identifying the compound. The investigation of this substance is being continued.

The photocatalytic synthesis of methylamine, pyridine, and piperidine is important, since it is analogous to that taking place in the living plant. As was shown in the first paper of this series, there are present in sunlight no rays of the very short wave-length necessary for the direct photosynthesis of the activated formaldehyde from carbonic acid. It was shown, however, that the synthesis takes place photocatalytically by the influence of visible light when the carbonic acid is in loose combination with a coloured base, such

as malachite green. In the present experiments, it has been shown that a similar photocatalytic synthesis takes place in visible light when the carbonic acid is associated with the coloured cupric ammonium complex. This synthesis, therefore, is another example of the mechanism which we believe to be that existing in the living plant, where the chlorophyll forms an additive compound with the carbonic acid, the activated formaldehyde being photosynthesised by the action of visible light on this coloured complex.

In order both to confirm our interpretation of these results and also to determine whether the synthesis proceeds further than the formation of the pyridine nucleus, we investigated the action of ultra-violet light on mixtures of ammonia and formaldehyde. In the first series of experiments, 1.3*M*-solutions of ammonia and formaldehyde were exposed to ultra-violet light for about one hundred and twenty hours. The resulting solutions were evaporated with excess of hydrochloric acid in order to remove the unused formaldehyde and finally taken to dryness. From the mixed hydrochlorides, by extraction with absolute alcohol and fractional precipitation by ether, in which methylamine hydrochloride is very sparingly soluble, specimens of nearly pure methylamine hydrochloride were obtained. The melting point was found to be 192—200°, and the chloroplatinate contained 40.8—41.1 per cent. of platinum (calculated, 41.68 per cent.), the low value being probably due to the presence of more complex bases which could not entirely be removed. Before dealing with these compounds, emphasis may again be laid on the fact that the total absence of α -amino-acids and of all reducing sugars was proved in these ammonia-formaldehyde solutions after exposure to light. If the relative amount of formaldehyde is very greatly increased, for example, 10 mols. to 1 mol. of NH_3 , then the presence of reducing sugars is readily identified after these solutions have been illuminated. It is also of considerable interest to note that no hexamethylenetetramine is formed.

In a second series of experiments with ammonia and formaldehyde, in which the period of illumination was more prolonged, further confirmation was obtained of the photosynthesis of pyridine, but in no case could we detect any evidence of piperidine. The separation of the pyridine hydrochloride from the methylamine hydrochloride was carried out in the following manner. The mixed hydrochlorides were digested with warm absolute alcohol, in which pyridine hydrochloride is much more soluble than methylamine hydrochloride. The alcoholic solution was treated with twice its volume of ether, which brought about the precipitation of the greater bulk of the methylamine hydrochloride. The filtrate was taken to dryness

and the residue extracted with a little chloroform, in which pyridine hydrochloride is very much more soluble than methylamine hydrochloride. On evaporation of the chloroform solution a very small quantity of almost pure pyridine hydrochloride was obtained. The normal chloroplatinate prepared from this had a melting point which was about 15° too low owing to its contamination with more complex bases of an alkaloidal nature.

Although the presence of an alkaloidal substance was proved by the reactions with all the usual reagents, sufficient material was not obtained in these experiments for its investigation. In order to examine this substance in greater detail experiments were carried out with stronger solutions. Twelve quartz tubes, each containing 100 c.c. of 2*M*-ammonia and formaldehyde, were exposed to ultra-violet light for three hundred hours. These solutions on exposure turned brown and on evaporation to dryness with hydrochloric acid and extraction with absolute alcohol a light brown solution was obtained which on evaporation deposited a brown, deliquescent solid with an odour resembling that of liquorice. A minute portion of this solid, when dissolved in water, gave very strong reactions with all the reagents for alkaloids, the most noteworthy being a heavy purplish-brown precipitate with a solution of iodine in potassium iodide, and a yellow precipitate and a characteristic odour on warming with Nessler's solution. It is this odour, also developed on treating the hydrochloride with alkali, that led us to suspect an alkaloid of the coniine group.

We therefore prepared as much as possible of the alkaloidal substance by exposing 2*M*-solutions of ammonia and formaldehyde to ultra-violet light for periods of six to ten days. The resulting solutions were worked up exactly as described above and a chloroform solution containing the pyridine and alkaloid hydrochlorides was obtained. On the addition of two volumes of ether to this solution, most of the pyridine hydrochloride was rapidly precipitated. On addition of a further small quantity of ether the remainder of the pyridine hydrochloride, together with a little alkaloid hydrochloride, separated. On evaporation of the second filtrate, a brown solid was obtained which on treatment with caustic alkali gave no odour of pyridine but only the characteristic odour of coniine. It would seem, therefore, that the alkaloid had been freed from pyridine by this treatment. The question of the relative amounts of these compounds will be dealt with below.

There is no doubt that the identification of coniine is a matter of considerable difficulty, and it is only after very careful investigation that we feel confidence in stating that our results go far towards proving the photosynthesis of this alkaloid from ammonia and

carbon dioxide. We have received great assistance from Dr. W. J. Dilling, who has made a study of this very matter, namely, the identification of coniine and its differentiation from its allies (*Pharm. J. and Pharmacist*, 1909, 4, 29), and we tender our most grateful thanks to him.

The most characteristic test for coniine is the crystalline precipitate which it gives with potassium cadmium iodide. A *neutral* solution of coniine hydrochloride, cooled in a freezing mixture, on cautious addition of the iodide solution, gives a white precipitate which under the microscope is found to consist of crystals shaped like an oak leaf. These characteristic crystals were obtained with our synthetic alkaloid and also with the natural alkaloid and found to be exactly similar in appearance. The conhydrines only give amorphous precipitates with this reagent.

The synthetic alkaloid on oxidation with potassium dichromate and sulphuric acid gave the unmistakable smell of butyric acid, no difference being found when the natural alkaloid was used in similar quantities.

Strong confirmatory evidence was obtained by Melzer's test (*Arch. Pharm.*, 1898, 236, 701) as modified by Dilling. One c.c. of a solution of the hydrochloride is made alkaline with sodium carbonate, 0.5 c.c. of alcohol and a few drops of carbon disulphide are then added, and the mixture is heated to the boiling point. Distilled water is then added until the test tube is two-thirds full, and afterwards a few drops of a saturated solution of uranium nitrate are added, when an orange-red colour is produced. On shaking with toluene or with ether, the coloured compound is extracted and the ethereal solution, on standing, deposits brown crystals. The solubility of the coloured compound in toluene definitely differentiates coniine from its allies and indeed is a specific test for coniine. In the case of the conhydrines, moreover, the ethereal solutions give amorphous deposits and not crystals. When nickel chloride is substituted for the uranium nitrate, a fine green colour is obtained, the substance being soluble in ether, which on standing deposits green crystals. This at once excludes γ -coniine, which gives a red colour with nickel chloride. With copper sulphate, the colour is Vandyck-brown, and opaque brown crystals are deposited from the ether. We obtained identical colours and crystals with our synthetic alkaloid and with natural coniine. These three tests are accepted as the best known for the identification of coniine, and in each case no difference whatever could be detected between the behaviour of our synthetic alkaloid and the natural alkaloid.

The picrate of the alkaloid was prepared and three specimens,

obtained in three separate syntheses, melted at $72-74^{\circ}$, $73-74.5^{\circ}$, and 74.5° , respectively. The melting point of the picrate of the natural alkaloid is differently recorded by various observers as lying between 74° and 76° , this no doubt being due to the fact that the picrate is amorphous. It is important to note that Ladenburg (*Ber.*, 1886, 19, 439, 2578) states that the melting point of the various compounds of synthetic 2-propylpiperidine are almost identical with those of the corresponding compounds of natural coniine. Although not much support can be derived from the melting point of the picrate, it can be stated that the melting point does not differ from that of the picrate of natural coniine, which we found to be very near 75° , but not sharp.

Ladenburg also found that the physiological action of his synthetic 2-propylpiperidine is identical with that of the natural alkaloid. The physiological action of our photosynthetic alkaloid was therefore examined in the following manner. After the brain and spinal cord of a frog had been pithed, the sciatic nerves and gastrocnemius muscles were dissected out and the right leg was tightly tied under the nerve to prevent circulation in this limb. The points at which these nerves and muscles responded when stimulated by the current from an induction coil with movable secondary were noted at intervals of time. The injection into the anterior lymph sac of 0.2 c.c. of a 5 per cent. solution of the synthetic alkaloid caused the response of the left sciatic nerve to become less and less until it finally ceased, although the right nerve and gastrocnemius muscle still responded. This effect is due to the paralysis of the motor nerve endings by the solution, an effect which is characteristic of coniine and its allies.

A second experiment was carried out for us by Dr. Dilling as follows. Two muscle-nerve preparations from a frog were fitted up, one in Ringer's solution and the other in Ringer's solution to which a small quantity of the hydrochloride of our photosynthesised alkaloid had been added. The accompanying tracing (facing p. 194) shows very clearly the characteristic paralysis of the nerve endings.

The experimental evidence obtained from the study of the reaction of the photosynthetic alkaloid would seem definitely to point towards its being coniine. The arguments may be summed up as follows. The physiological action is very characteristic and is one which is given *only* by the curare alkaloids and by the members of the coniine group, and since the former are definitely excluded by the total failure of the characteristic tests for these alkaloids the results shown in the tracing can only have been given by an alkaloid of the coniine group. This conclusion is supported by the chemical reactions which are very characteristic of this group.

As stated above, we are fully aware of the difficulty of the identification of coniine, but on the results of the tests which are universally recognised as being the best for the differentiation of coniine from its allies we feel confident in stating that the evidence is markedly in favour of the photosynthetic alkaloid being coniine itself. The crystalline nature of the double salt obtained on the addition of potassium cadmium iodide solution and the solubility

DESCRIPTION OF PLATE.

FIG. 1.—Upper tracing: Muscle immersed in bath of Ringer's solution as control. Lower tracing: Muscle immersed in bath of 0.4% synthetic coniine in Ringer's solution. Sciatic nerves of both muscles rest on electrodes through which a galvanic break stimulus passes every 5 seconds. Coil distance = 11 cm. The tracing shows rapid onset of fatigue in the case of the poisoned muscle owing to paralysis by the coniine of the myoneural junctions of the sciatic nerve. At arrow, muscles immersed in bath.

FIG. 2.—Continuation of Fig. 1. Coil distance reduced to 5 cm. Shows paralysis of myoneural junctions of sciatic nerve.

FIG. 3.—After 3 minutes' rest. Normal muscle-nerve preparation responds to stimulus. Coil distance = 11 cm. No recovery of the poisoned preparation after rest; therefore it is not a simple fatigue effect.

FIG. 4.—Still no recovery of poisoned muscle-nerve preparation. Complete paralysis of myoneural junctions of sciatic nerve even to strong stimulus. Coil distance = 2 cm.

FIG. 5.—Ten minutes after Fig. 4. Upper tracing: Normal muscle-nerve preparation stimulated through sciatic nerve. Lower tracing: Poisoned muscle-nerve preparation stimulated directly through muscle, showing that muscle is not paralysed.

FIG. 6.—Five minutes after Fig. 5. Both preparations stimulated through muscle. Coil distance = 7 cm.

The object of the experiment is to show that the coniine paralyses the endings (myoneural junctions) of voluntary motor nerves without paralysing the muscle fibres. In Fig. 1, the poisoned muscle rapidly becomes inexcitable by a stimulus applied to the nerve because owing to the paralysis of the myoneural junction the stimulus applied to the nerve is "blocked" or is unable to reach the contractile elements of the muscle. But, as Figs. 5 and 6 show, the contractile elements of the muscle itself are not paralysed, because they are still excitable by a stimulus directly applied to the muscle substance.

in toluene of the red compound obtained with uranium nitrate in Melzer's test are reactions only given by coniine and not by any other known member of the group. Furthermore, the photosynthetic alkaloid and the natural alkaloid are exactly similar in all their properties and reactions. Certain other tests might be suggested, but in view of the fact that the reactions we have employed are those specially selected after lengthy research as being the only ones in which confidence can be placed, we feel that the

22 Action on Gastrocnemius Muscle, *in vivo*, of *Bombesin* of Synthetic Alkaloid-Containing
0.1 per cent. in Ringer's Solution.

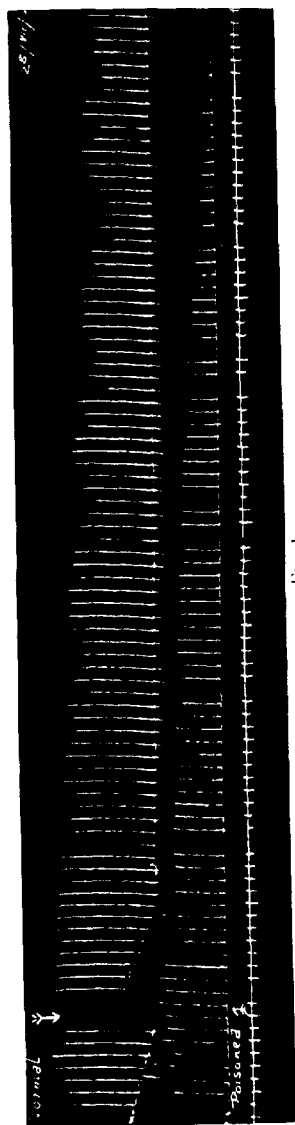


FIG. 1.



FIG. 2.



FIG. 3.



FIG. 4.



FIG. 5.

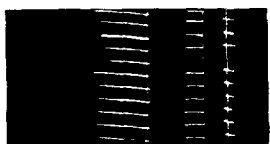


FIG. 6.

argument in favour of the photosynthesis of coniine would not be materially strengthened by their use.

Reference may be made to the detection of pyridine and piperidine recorded above. It must be noted that these compounds form an intermediate stage in the synthesis of the coniine alkaloid and therefore they are only obtained in very small quantities. If the times of exposure to the light are increased, the quantity of pyridine or piperidine found in the solution is not materially increased and the difficulties of the work become much greater owing to the formation of the alkaloid. It may, however, be stated that in certain analogous photosyntheses at present under investigation we have obtained indisputable evidence of the synthesis of both these compounds, and we hope to communicate these results in a further paper.

We consider that it is by no means out of place to refer once again to the peculiar difficulties of these photosynthetic investigations. In the first place, the initial substance produced is activated formaldehyde, which contains an abnormally large quantity of energy. The subsequent processes consist in the reaction between this compound and other substances, each process being a series of reactions in which energy is lost. In the investigation now described, the last stage reached is an alkaloid, which is most probably coniine. The compounds formed as intermediates between the first and final stages will obviously only exist in the free state for a short period of time, since they will immediately undergo further reaction. The pyridine and piperidine are intermediates and only have a transient existence, or in other words they will at any given moment only be present in very small quantities.

A second difficulty is found in the fact that the more complex products of the photosynthesis are slowly decomposed by light of very short wave-length. Whilst it might, for instance, be thought possible to synthesise considerable quantities of the coniine alkaloid by exposing the solutions for very long periods to ultra-violet light, this is not feasible, since the alkaloid is slowly decomposed. Not only does this militate against a good yield, but it also introduces further difficulties owing to the formation of decomposition products. It is scarcely necessary to point out that this factor is absent in the living plant, and we have not as yet succeeded in devising an effective screen to absorb the very short wave-length rays and transmit the rays required for the formation of the activated formaldehyde.

In the present experiments we have investigated the photosynthesis step by step, each stage being separately studied. The first stage is the production of activated formaldehyde by the

action of light on aqueous solutions of carbonic acid. This was dealt with in the first paper of this series, and we have now found another example of the photocatalysis of this reaction. In the second stage, the first product to appear in quantities sufficient for its recognition, except, of course, the nitric acid, is methylamine, and its presence can be detected very soon after the solutions have been exposed to the light.

If the times of exposure are increased, pyridine or piperidine makes its appearance, and it would at first sight seem probable that they are synthesised by the action of the activated formaldehyde on the methylamine, but this conclusion is by no means certain. Pyridine and piperidine might well be formed by direct synthesis from five molecules of formaldehyde and one molecule of ammonia, the delay in the appearance of these compounds in sufficient quantity for their recognition being due to the fact that with a given velocity of formation of activated formaldehyde only one pyridine nucleus would be formed to five molecules of methylamine. There is also to be noted the significant fact that no compounds intermediate between methylamine and pyridine, for example, dimethylamine, ethylamine, have been found. So far as the present evidence is able to help us, it is more in favour of the direct nuclear synthesis from ammonia and formaldehyde than the synthesis with methylamine as the first stage. Whichever of these alternatives is correct, all three substances, methylamine, pyridine, and, probably, piperidine, have been photosynthesised by the action of ultra-violet light of short wave-length on aqueous solutions of ammonia saturated with carbon dioxide, and photocatalytically synthesised by the action of visible light on ammoniacal solutions of cupric carbonate, saturated with carbon dioxide.

In order to carry out the next step, namely, the photosynthesis of the coniine, greater reaction velocity is required. Solutions of ammonia and formaldehyde, 2*M* with respect to each, were exposed to ultra-violet light for six to ten days. The progress of the photosynthesis is the same in this case, since we have found that methylamine is the first product and that pyridine can be detected subsequently. The formation of the coniine takes place after the production of the pyridine, and therefore it is doubtless synthesised by the action of the activated formaldehyde on pyridine.

We consider that the present results support the conclusions drawn in the preceding paper. In this connexion it is important to note that when the ammonia-carbon dioxide solutions, after exposure to ultra-violet light, are evaporated under reduced pressure, the whole of the methylamine, pyridine, piperidine, and excess of ammonia is distilled off and that the residual solution in the dis-

tilling flask contains no sugars or amino-acids. In our opinion, this militates against any proposal that the photosynthesis takes place along paths of greater complexity, such, for example, as that of amino-acids. Indeed, the results now brought forward would seem to confirm the views we expressed in the previous paper as to the simplicity of the photosynthesis which takes place when activated formaldehyde is produced in the presence of potassium nitrite or ammonia.

In conclusion, we once again express our most cordial thanks to Dr. W. J. Dilling for his kindness in carrying out part of the physiological work and for the readiness with which he placed at our disposal his great knowledge of coniine and its differentiation from the other members of this group.

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[Received, October 19th, 1922.]

XXIV.—*The Velocity of Reaction in Mixed Solvents.* *Part IV. The Influence of the Base on the Velocity* *of Saponification of Esters.*

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ARCHIBALD SCARBOROUGH.

IN previous communications (T., 1921, **119**, 970; 1922, **121**, 243, 2308), a systematic study has been made of the reaction between the ethyl esters of typical aliphatic and aromatic monobasic acids and potassium hydroxide in a series of solvent media consisting of ethyl alcohol and water, and also of the effect due to a rise or fall in the temperature at which the reaction proceeds. The results showed that the curve exhibiting the relation between the velocity constant and the percentage composition of the solvent was divisible into not fewer than four linear phases; the points of intersection of these phases were usually well defined and corresponded with alcohol-water complexes of simple composition. These points of intersection were found to be independent of the nature of the ester, except in the case of the ortho-substituted aromatic esters, where one of the points of intersection became much more sharply defined and was found to occur at 62.5 per cent. of alcohol instead of at 59 per cent. of alcohol, as was the case with all other esters. The influence of a change of temperature of 30° was apparently to eliminate certain points of intersection and to introduce others, so that it would seem that certain complexes possessed little stability or that their effect was reduced to

such an extent that the methods employed failed to detect their presence.

The effect of the temperature and of the ester on the velocity constant having been determined, it seemed of interest to examine the effect due to a change of base. Measurements have therefore been made of the velocity of reaction of the ethyl esters of an aliphatic, an aromatic, and an ortho-substituted aromatic acid with lithium hydroxide, with barium hydroxide, and with tetraethylammonium hydroxide at 30°. In the case of barium hydroxide, the solubility of the base in a solvent medium containing more than 40 per cent. of alcohol was so small that the reaction mixture became non-homogenous as the reaction proceeded and the value of the velocity constant was too irregular to have any exact significance.

An examination of the results shows that the curves have certain characteristics independent of the nature of the base, but the positions of the points of intersection of the phases are not common to all bases, and only in those phases which are common can the ratios $k_{\text{KOH}}/k_{\text{base}}$ be calculated. In the following table are shown the results obtained for the three esters and bases examined :

TABLE I.

Per cent. alcohol.	Ethyl benzoate.		Ethyl isobutyrate.		Ethyl o-bromobenzoate.	
	$\frac{k_{\text{KOH}}}{k_{\text{LiOH}}}$	$\frac{k_{\text{KOH}}}{k_{\text{NEt}_4\text{OH}}}$	$\frac{k_{\text{KOH}}}{k_{\text{LiOH}}}$	$\frac{k_{\text{KOH}}}{k_{\text{NEt}_4\text{OH}}}$	$\frac{k_{\text{KOH}}}{k_{\text{LiOH}}}$	$\frac{k_{\text{KOH}}}{k_{\text{NEt}_4\text{OH}}}$
90	1.07	1.40	1.16	1.51	1.54	3.14
85	1.09	1.31	1.20	1.36	1.47	2.32
80	1.15	1.38	1.22	1.41	1.66	2.35
75	—	1.28	—	1.27	—	—
70	1.10	1.30	1.02	1.29	1.16	1.81
40	1.20	1.26	1.00	1.10	1.14	1.25
35	1.15	1.24	1.03	1.05	1.10	1.21
30	1.04	1.25	1.11	1.28	1.00	1.31
Mean	1.10	1.30	1.10	1.30	1.08	1.25

The curve for ethyl o-bromobenzoate with potassium hydroxide appears to be quite different from those obtained with the other bases, and a comparison is only possible over the one phase as shown.

A closer consideration of the results and of the curves shows that the critical points for the three bases, examined in detail, are as follow :

TABLE II.

Base.	Critical points (per cent. of alcohol) at 30°.			
KOH	80.5	59*		30.5
LiOH	81		46	
NEt ₄ OH	„	62—60	„	„

* For esters of ortho-substituted acids this value becomes 62.5.

The existence of the various linear phases has been verified by applying the method of mean squares to the experimental data, and, as will be seen from the following table, the discrepancy between theory and observation is within the limit of experimental error.

TABLE III.

Ethyl isobutyrate and lithium hydroxide.			Ethyl benzoate and tetraethylammonium hydroxide.		
Per cent. alcohol.	k_{obs}	k_{calc}	Per cent. alcohol.	k_{obs}	k_{calc}
80	0.076	0.073	45	0.179	0.177
70	0.114	0.119	40	0.230	0.229
60	0.168	0.165	35	0.287	0.286
50	0.212	0.212	30	0.341	0.340

The curves for lithium hydroxide at 30° show a marked similarity to those obtained with potassium hydroxide at 45°, where it was shown that the value of k in 50 per cent. alcohol occurred in the same phase as those in 80, 70, and 60 per cent. alcohol. The evidence points strongly to the existence of a complex represented by the formula $C_2H_5\cdot OH, 3H_2O$ and having the composition 46 per cent. of alcohol.

The curves obtained with tetraethylammonium hydroxide appear to combine the characteristics of those of lithium hydroxide and potassium hydroxide in that a marked discontinuity occurs at 60 per cent. of alcohol as well as at 46 per cent. of alcohol.

It is thus seen that the points of intersection occurring at 80 and 30 per cent. alcohol are independent of the nature of the base, of the ester, and of the temperature. On the other hand, the points of intersection at 62.5, 59, 46, and 39 per cent. alcohol are dependent on the temperature and the nature of the ester or of the base.

The results obtained with barium hydroxide are of too low an order of accuracy to make a detailed study possible; they are, however, sufficiently accurate to show that the base is twice as reactive as potassium hydroxide in solvents containing a high percentage of alcohol, and that as the percentage of water is increased the reactivity decreases until it is nearly the same as that of potassium hydroxide.

TABLE IV.

Ethyl *p*-chlorobenzoate and barium hydroxide.

Per cent. alcohol	...	85	80	70	60	40	35	30
k_{KOH}/k_{BaOH_2}	0.43	0.54	0.62	0.72	0.77	0.72	0.82

The results recorded in this and in the previous communications (*loc. cit.*), and also data relating to the physical properties of ethyl alcohol-water mixture, seem to show that we are dealing with effects due to the solvent existing as an equilibrium mixture of which one component is an alcohol-water complex.

It might be expected that the existence of these alcohol-water complexes would be shown by the saponification of any ester by a base in alcohol-water mixtures, irrespective of the nature of the base; but this does not appear to be the case. If it is assumed that the reaction is promoted by the hydroxyl-ions of a base—in equivalent dilutions, the concentration of hydroxyl-ions will not be greatly different for strong bases—then the effect of the alcohol-water complex should be shown in the presence of any strong base. Thus the possibility of the saponification of an ester being due mainly to the presence of hydroxyl-ions appears to be eliminated. In this connexion, it is interesting to note that Acree (*J. Amer. Chem. Soc.*, 1915, **37**, 1902, 1909; 1917, **39**, 376) finds that even in absolute ethyl alcohol the reaction between dinitrobenzene or an alkyl haloid and a base is partly ionic in character.

The alternative explanation seems to be that the reaction is molecular and that the different results found with the three bases are due to some loose combination of the base and the alcohol-water complexes; each base may be supposed to exert a selective action upon the alcohol-water complex with which it enters into combination.

A noticeable feature of the work described in this paper is the order found for the reactivity of the bases; the reactivity decreases as we pass from barium hydroxide, potassium hydroxide, lithium hydroxide, to tetraethylammonium hydroxide. Measurements of the relative strengths of bases in aqueous solution by a comparison of the rates at which an ester is saponified have been carried out (Reicher, *Annalen*, 1885, **228**, 257; 1886, **232**, 103; Bugarsky, *Z. physikal. Chem.*, 1891, **8**, 398) and the order in decreasing stages of reactivity is: lithium hydroxide, potassium hydroxide, barium hydroxide, and tetraethylammonium hydroxide.

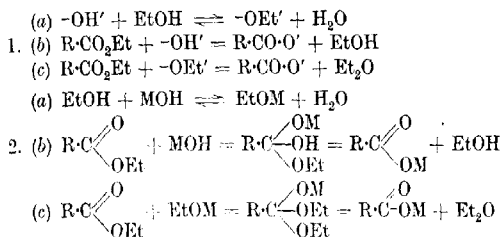
It seems desirable at this stage to offer some explanation of these results.

The equation representing the reaction between the ester of a monocarboxylic acid and a base is usually represented as



which is entirely inadequate as an explanation of the mechanism of the reaction in solvents consisting of alcohol-water mixtures.

Under these conditions, the mechanism of the reaction may be represented by two alternative sets of equations:



where R is an alkyl or aryl radicle and M is an electropositive radicle.

In order to bring the results into accord with the first series of equations, it must be assumed that, in equivalent dilute solutions of barium hydroxide and potassium hydroxide, the concentration of the negative or active ion of the former base is twice that of the latter. In very dilute aqueous solutions, however, the concentration of hydroxyl-ion will be nearly the same for both bases; therefore in ethyl alcohol, a solvent of lower ionising power, the weaker base would be less highly ionised than the stronger base. These two conflicting statements may be brought into agreement if two possibilities are conceded:

(1) That the hydroxyl-ion is considerably more reactive than the ethoxyl-ion.

This possibility is in agreement with the experimental evidence.

(2) That the balanced reaction 1(a) proceeds so much further towards the right in the case of potassium hydroxide than in the case of barium hydroxide that the concentration of hydroxyl-ions in the latter case is some two to three times that in the case of potassium hydroxide.

The second series of equations assumes that the reaction proceeds in stages, the first of which is a slow bimolecular reaction resulting in the formation of a complex, which then decomposes more rapidly and in accordance with an equation for a unimolecular reaction. The isolation of a complex of this nature by von Pechmann (*Ber.*, 1898, **31**, 501) lends support to this view. As is evident from equation 2(c), the reaction is complicated by the formation of a metallic ethoxide: the extent to which this takes place in any alcohol-water mixture is not known, neither is there any precise knowledge of the relative rates of decomposition of the complexes indicated in equations 2(b) and 2(c), but it is believed that the latter complex breaks down much more slowly than the former (*vide* Gennari, *Gazzetta*, 1896, **26**, i, 231; Kremann, *Monatsh.*, 1905, **26**, 279).

The reactivity of the various hydroxides in ethyl alcohol-water mixtures is thus apparently a measure of the amount of free hydroxide present as such in the solution or, alternatively, a measure of the hydroxyl-ion concentration. From the results it may be deduced that the relative reactivities of the bases in alcohol-water mixtures containing a high percentage of alcohol are



If a correction is made for the relative strengths of the bases in aqueous solution, these values become



The amount of free hydroxide present in the alcohol-water mixtures should be nearly proportional to the first series of numbers; the relative rates of reaction of the bases with a given ester should be nearly proportional to the second series of numbers.

There is some difficulty in testing the above suppositions in the case of ethyl alcohol, but indirect evidence may be obtained from the work of Cajola (*Gazzetta*, 1900, 30, i, 233); in this work, a study was made of the velocity of reaction between methyl acetate and various bases in equivalent concentrations in absolute methyl alcohol. The reaction was found not to be strictly bimolecular, and appeared to cease before the ester was completely saponified. The amount of ester saponified by one equivalent of the following bases was:

NaOH	NH ₃	KOH	NMe ₄ OH	Ba(OH) ₂
13	23	26	32.5	52

No explanation of these figures was put forward, but it seems possible that they represent the amount of free hydroxide present, and that the reaction ceases for one of the following reasons:

(a) The complex formed between the methoxide and the ester in methyl alcoholic solution is very stable compared with the analogous complex formed in ethyl alcoholic solution.

(b) The equilibrium represented by the equation $\text{CH}_3\text{OH} + \text{MOH} \rightleftharpoons \text{CH}_3\text{OM} + \text{H}_2\text{O}$ is incapable of readjusting itself with sufficient speed for the reaction to proceed to a conclusion or even to appear as a truly bimolecular reaction, owing to the extreme stability of the methoxide.

The work of von Pechmann tends to confirm (a) and this is supported by the fact that the complex formed between ethyl benzoate and potassium hydroxide is so unstable that it cannot be isolated under conditions comparable with those employed with the corresponding methyl complex.

Making these assumptions, it is possible to obtain the following figures representing the relative amount of hydroxide present as such in methyl-alcoholic solution :



If a correction is made for the relative strengths of the bases in aqueous solution, the following figures are obtained :



This series shows remarkable agreement with the results obtained in ethyl alcohol-water mixtures, but too much significance must not be attached to these figures, as comparisons depending on analogous properties of methyl and ethyl alcohols are not always trustworthy.

It seems possible that an extension of the work of Cajola might yield evidence as to the validity of some of the views which have been put forward. Some preliminary experiments have already been carried out and these tend to confirm Cajola's results.

EXPERIMENTAL.

The solvents and the esters were prepared in the usual manner. The experiments with lithium hydroxide were carried out in the manner described for potassium hydroxide; the lithium hydroxide was an A.R. specimen. The experiments were carried out at 30°.

The tetraethylammonium hydroxide was obtained as a 10 per cent. aqueous solution from two sources (Kahlbaum, Schuchardt). An alcohol-water solution of the base was made by taking a known weight of an alcohol-water mixture containing a higher percentage of alcohol than that to be used in the experiment and adding from a burette the quantity of a 10 per cent. aqueous solution of the base required to reduce the percentage of alcohol to that to be used in the experiment. From a determination of the density of the aqueous solution of the base, it was calculated that 10 c.c. of the solution corresponded with 10 grams of water. The normality of the base in this solution was then determined by titration and the mixture was diluted, if necessary, by adding an alcohol-water mixture containing the same percentage of alcohol.

Under the same conditions, the two samples of the 10 per cent. solution of the base gave identical results. It was shown by control experiments that this method of preparing the alcohol-water solutions of the tetraethylammonium hydroxide gave results well within the experimental error.

The alcohol-water solutions of barium hydroxide were made by

gently boiling the solvent with an excess of the base, cooling, and drawing the supernatant liquid through a glass wool filter into a storage vessel. Measured quantities of the solution were obtained by means of a burette connected with the storage vessel. Throughout the various stages, the solution was protected from contamination with carbon dioxide by means of soda-lime tubes. A control experiment showed that the ethyl alcohol-water mixtures subjected to these processes suffered no appreciable change in density.

The results are shown in the following tables and curves :

TABLE V.

Lithium hydroxide and ethyl benzoate.

Per cent. alcohol.	C_{LiOH} .	C_{ester} .	Limit k .	k .
90	0.05370	0.02500	0.0435—0.047	0.0455
85	0.04675	0.03333	0.056—0.060	0.058
82.5	0.04667	0.02917	0.059—0.064	0.063
80	0.04721	0.03333	0.072—0.077	0.074
70	0.05721	0.02222	0.104—0.112	0.108
60	0.05340	"	0.131—0.145	0.136
55	0.04062	0.01875	0.146—0.154	0.150
50	0.03946	0.01644	0.156—0.169	0.163
47.5	0.04096	0.01666	0.195—0.21	0.200
45	0.04330	0.01875	0.195—0.23	0.210
42.5	0.03880	0.01666	0.217—0.230	0.225
40	0.04155	"	0.237—0.249	0.241
35	0.03495	"	0.30—0.325	0.31
30	0.05236	"	0.405—0.43	0.41
25	0.01091	0.00453	0.72—0.76	0.745
20	0.00777	0.00429	1.03—1.23	1.12

TABLE VI.

Lithium hydroxide and ethyl isobutyrate.

Per cent. alcohol.	C_{LiOH} .	C_{ester} .	Limit k .	k .
90	0.05370	0.02500	0.042—0.0445	0.043
85	0.04675	0.03333	0.058—0.062	0.059
82.5	0.06403	0.03479	0.069—0.0735	0.0715
80	0.06164	0.03333	0.0745—0.0785	0.076
70	0.04314	0.02777	0.109—0.118	0.114
60	0.06261	0.02222	0.162—0.173	0.168
55	0.03802	0.01666	0.180—0.195	0.187
50	0.04590	"	0.207—0.215	0.212
47.5	0.03905	0.01875	0.267—0.281	0.275
45	0.03739	0.01666	0.280—0.312	0.295
42.5	0.03880	"	0.315—0.33	0.32
40	0.02066	0.01111	0.345—0.365	0.355
35	0.03495	0.01666	0.415—0.44	0.42
30	0.05238	"	0.51—0.55	0.53
25	0.01091	0.00453	0.77—0.86	0.82
20	0.00777	0.00429	1.03—1.23	1.12

TABLE VII.
Lithium hydroxide and ethyl *o*-bromobenzoate.

Per cent. alcohol.	C_{LiOH}	C_{ester}	Limit k .	k .
90	0.06333	0.03333	0.056—0.060	0.059
85	0.04967	"	0.065—0.069	0.068
82.5	0.06403	0.03479	0.0795—0.085	0.080
80	0.06164	0.03333	0.0795—0.084	0.0815
70	0.04314	0.02222	0.102—0.114	0.106
60	0.06261	"	0.118—0.132	0.126
55	0.03802	0.01666	0.127—0.136	0.130
50	0.03907	"	0.130—0.144	0.139
47.5	0.04096	"	0.154—0.168	0.160
45	0.03330	"	0.163—0.182	0.173
42.5	0.03880	"	0.178—0.186	0.184
40	0.02066	0.00833	0.185—0.205	0.192
35	0.02620	0.01111	0.221—0.240	0.234
30	0.02924	"	0.31—0.34	0.33

TABLE VIII.
Tetraethylammonium hydroxide and ethyl benzoate.

Per cent. alcohol.	C_{NEt_4OH}	C_{ester}	Limit k .	k .
90	0.02697	0.02222	0.0315—0.0335	0.0325
85	0.03235	0.02500	0.045—0.050	0.0485
82.5	0.03031	"	0.054—0.057	0.0555
80	0.04554	"	0.058—0.064	0.0615
75	0.04178	"	0.070—0.074	0.073
70	0.04981	0.02272	0.080—0.083	0.0815
65	0.04793	0.02500	0.092—0.095	0.094
60	0.05194	0.02222	0.119—0.127	0.124
55	0.04082	0.01666	0.128—0.132	0.130
50	0.04445	"	0.136—0.141	0.139
47.5	0.03955	0.02222	0.156—0.165	0.161
45	0.04574	"	0.173—0.185	0.179
40	0.03701	0.01666	0.221—0.239	0.230
35	0.02276	0.01333	0.270—0.290	0.280
30	0.02078	0.01111	0.33—0.355	0.34
25	0.00778	0.00458	0.50—0.54	0.52
20	0.00706	0.00409	0.785—0.82	0.80

TABLE IX.
Tetraethylammonium hydroxide and ethyl isobutyrate.

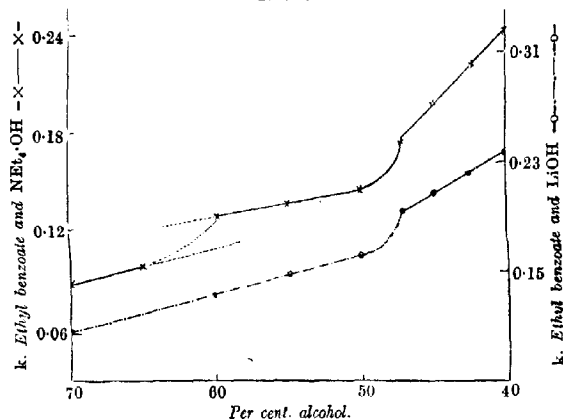
Per cent. alcohol.	C_{NEt_4OH}	C_{ester}	Limit k .	k .
90	0.02697	0.02222	0.032—0.0335	0.0325
85	0.03235	0.02500	0.051—0.0525	0.052
82.5	0.03031	"	0.0575—0.060	0.059
80	0.02719	"	0.065—0.068	0.066
75	0.04178	"	0.079—0.083	0.082
70	0.04556	"	0.089—0.093	0.090
65	0.04793	"	0.108—0.114	0.110
60	0.05194	0.02222	0.144—0.153	0.148
55	0.04082	0.01666	0.166—0.173	0.170
50	0.04445	"	0.185—0.192	0.190
47.5	0.03955	0.02222	0.214—0.226	0.221
45	0.03430	0.02500	0.235—0.248	0.245
40	0.03701	0.01666	0.31—0.325	0.320
35	0.02276	0.01333	0.39—0.415	0.405
30	0.02078	0.01111	0.45—0.48	0.47
25	0.00778	0.00458	0.675—0.70	0.69
20	0.00947	"	0.84—0.865	0.85

TABLE X.

Tetraethylammonium hydroxide and ethyl *o*-bromobenzoate.

Per cent. alcohol.	$\text{CNEt}_4\cdot\text{OH}$.	C_{ester} .	Limit k .	k .
90	0.02697	0.02222	0.028—0.030	0.029
85	0.03235	0.02500	0.042—0.044	0.043
82.5	0.03031	"	0.0485—0.052	0.051
80	0.02719	"	0.052—0.054	0.0525
75	0.04166	"	0.0625—0.065	0.064
70	0.05588	"	0.0675—0.0705	0.0685
65	0.04711	0.03333	0.077—0.080	0.0785
60	0.05194	0.02222	0.094—0.098	0.097
55	0.04082	0.01666	0.099—0.103	0.101
50	0.02976	0.02222	0.101—0.107	0.104
47.5	0.03955	"	0.121—0.126	0.124
45	0.03430	0.02500	0.132—0.139	0.134
40	0.02776	0.01250	0.175—0.185	0.180
35	0.02171	0.01111	0.21—0.23	0.215
30	0.02078	0.00833	0.24—0.26	0.245

FIG. 1.

*Summary.*

1. The reaction between the ethyl esters of certain monobasic acids and certain hydroxides in a solvent consisting of alcohol and water is found to be of the second order and independent of the concentrations.

2. Under the same conditions, the velocity of reaction decreases as the base is changed in the following order: Barium hydroxide, potassium hydroxide, lithium hydroxide, tetraethylammonium hydroxide.

3. The relative velocities of reaction are not in agreement with the relative strengths of the bases in aqueous solution, but appear to be some function of their relative strengths and of their power to form ethoxides.

4. The curve exhibiting the relation between k and the composition of the solvent shows certain common characteristics for all the bases examined. The critical points corresponding with alcohol-water complexes are not identical for all bases.

5. The alcohol-water complexes represented by the compositions 80 and 30 per cent. of alcohol are independent of the nature of the ester, base, and of the temperature.

The authors wish to thank the Royal Society for a grant which has enabled this work to be carried out; one of us (A. E. C.) is indebted to the Department of Scientific and Industrial Research for a grant, for which he desires to express his thanks.

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[Received, November 8th, 1922.]

TABLE VII.
Lithium hydroxide and ethyl *o*-bromobenzoate.

Per cent. alcohol.	C_{LiOH}	C_{ester}	Limit k .	k .
90	0.06533	0.03333	0.056—0.060	0.059
85	0.04967	"	0.065—0.069	0.068
82.5	0.06403	0.03479	0.0795—0.085	0.080
80	0.06164	0.03333	0.0795—0.084	0.0815
70	0.04314	0.02222	0.102—0.114	0.106
60	0.06261	"	0.118—0.132	0.126
55	0.03802	0.01666	0.127—0.136	0.130
50	0.03907	"	0.130—0.144	0.139
47.5	0.04096	"	0.154—0.168	0.160
45	0.03739	"	0.163—0.182	0.173
42.5	0.03880	"	0.178—0.186	0.184
40	0.02966	0.00833	0.185—0.205	0.192
35	0.02620	0.01111	0.221—0.240	0.234
30	0.02924	"	0.31—0.34	0.33

TABLE VIII.
Tetraethylammonium hydroxide and ethyl benzoate.

Per cent. alcohol.	C_{NEt_4OH}	C_{ester}	Limit k .	k .
90	0.02697	0.02222	0.0315—0.0335	0.0325
85	0.03235	0.02500	0.0475—0.050	0.0485
82.5	0.03031	"	0.054—0.057	0.0555
80	0.04554	"	0.058—0.064	0.0615
75	0.04178	"	0.070—0.074	0.073
70	0.04981	0.02272	0.080—0.083	0.0815
65	0.04793	0.02500	0.092—0.095	0.094
60	0.05194	0.02222	0.119—0.127	0.124
55	0.04082	0.01666	0.128—0.132	0.130
50	0.04445	"	0.136—0.141	0.139
47.5	0.03955	0.02222	0.156—0.165	0.161
45	0.04574	"	0.173—0.185	0.179
40	0.03701	0.01666	0.221—0.239	0.230
35	0.02276	0.01333	0.270—0.290	0.280
30	0.02078	0.01111	0.33—0.355	0.34
25	0.00778	0.00458	0.50—0.54	0.52
20	0.00706	0.00409	0.785—0.82	0.80

TABLE IX.
Tetraethylammonium hydroxide and ethyl *isobutyrate*.

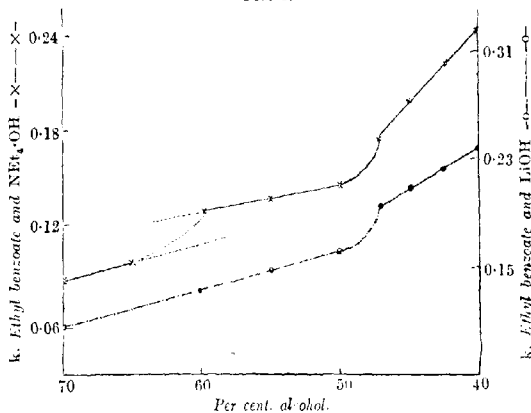
Per cent. alcohol.	C_{NEt_4OH}	C_{ester}	Limit k .	k .
90	0.02697	0.02222	0.032—0.0335	0.0325
85	0.03235	0.02500	0.051—0.0525	0.052
82.5	0.03031	"	0.0575—0.060	0.059
80	0.02719	"	0.065—0.068	0.066
75	0.04178	"	0.070—0.083	0.082
70	0.04556	"	0.089—0.093	0.090
65	0.04793	"	0.108—0.114	0.110
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40	0.03701	0.01666	0.31—0.325	0.320
35	0.02276	0.01333	0.39—0.415	0.405
30	0.02078	0.01111	0.45—0.48	0.47
25	0.00778	0.00458	0.675—0.70	0.69
20	0.00947	"	0.84—0.865	0.85

TABLE X.

Tetraethylammonium hydroxide and ethyl *o*-bromobenzoate.

Per cent. alcohol.	CNEt_4OH .	Center-	Limit <i>k</i> .	<i>k</i> .
90	0.02697	0.02222	0.028—0.030	0.029
85	0.03235	0.02500	0.042—0.044	0.043
82.5	0.03031	"	0.0485—0.052	0.051
80	0.02719	"	0.052—0.054	0.0525
75	0.04166	"	0.0625—0.065	0.064
70	0.05588	"	0.0675—0.0705	0.0685
65	0.04711	0.03333	0.077—0.080	0.0785
60	0.05194	0.02222	0.094—0.098	0.097
55	0.04082	0.01666	0.099—0.103	0.101
50	0.02976	0.02222	0.101—0.107	0.104
47.5	0.03955	"	0.121—0.126	0.124
45	0.03430	0.02500	0.132—0.139	0.134
40	0.02776	0.01250	0.175—0.185	0.180
35	0.02171	0.01111	0.21—0.23	0.215
30	0.02078	0.00833	0.24—0.26	0.245

FIG. 1.

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[Received, November 8th, 1922.]

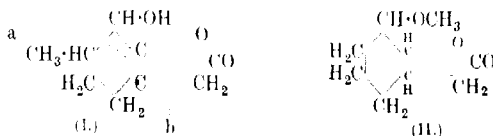
XXV.—*Castelamarin*—A Bitter Principle from *Castela Nicholsoni*.

By LOUIS PIERRE BOSMAN.

It has already been shown that castelamarin occurs, together with the glucoside castelin, in *Castela Nicholsoni* (T., 1922, 121, 970). Prof. George Barger kindly presented the author with a few specimens of impure castelamarin. After a prolonged series of experiments it was found that the substance was best purified either from 60 per cent. alcohol or by dissolving it in warm water to which a few drops of caustic soda solution had been added and reprecipitating it with dilute hydrochloric acid. The author found that the latter process gave a better yield.

EXPERIMENTAL.

0.5 Gram of the impure castelamarin, when dissolved in warm alcohol, yielded 0.31 gram of the pure substance, which crystallised in aggregates of thin needles. Repeated attempts to recover a further quantity from the mother-liquors were without result. 0.2710 Gram of the impure substance was dissolved in 10 c.c. of warm water to which three drops of 40 per cent. sodium hydroxide were added. It was *slowly* reprecipitated by a little dilute hydro-



The molecule, on breaking up (when oxidised) along *ab*, would give rise to a dicarboxylic acid—possibly a substituted succinic acid.

Hydrolysis of Castelamarin.—Purified castelamarin (1.48 grams) was heated under reflux for four hours with 120 c.c. of 2½ per cent. sulphuric acid. Within forty-five minutes the substance had completely dissolved. The solution was extracted three times with 70 c.c. of ether. The extracts left a resinous residue interspersed with crystalline leaflets. Further extractions with chloroform yielded practically nothing. Numerous solvents and mixtures of solvents were tried as crystallising media for this residue, but from ethyl acetate alone was it possible to obtain a minute quantity of a needle-like, crystalline product, which melted at 166–168°, gave no coloration with concentrated sulphuric acid, and was soluble in alcohol, ethyl acetate, or warm chloroform.

The acid solution from the ethereal and chloroformic extractions was neutralised with barium hydroxide, and the clear filtrate examined; save the fact that it had powerful reducing properties, nothing can be reported.

Oxidation of Castelamarin.—Experiments with acid and alkaline potassium permanganate and with dilute nitric acid (1 : 3) showed that the last is the best oxidising agent. Castelamarin (0.4 gram), heated on the water-bath with 10 c.c. of dilute nitric acid, dissolved in about fifteen minutes. The cooled solution was neutralised and extracted with chloroform. The residue after evaporation of the solvent was most conveniently recrystallised from 80 per cent. alcohol, from which it separated in well-defined needles, which melted at 238–240°, developed no coloration with concentrated sulphuric acid, and did not give the fluorescein reaction. The quantity of material was too small for further examination.

Pharmacological Action of Castelamarin.—A series of experiments on isolated tissues and tissues *in situ* were tried, but almost all the results were negative. Strengths of solutions up to 1 : 500 were used, but had no effect on the isolated intestine and uterus of a non-pregnant cat. The increase in tone was so small as to be practically negligible.

The most striking effect of a perfusion of an isolated mammalian heart with a 1 : 2000 solution of castelamarin was the constriction of the coronary vessels. This was indicated by the great retardation of the coronary outflow, which was reduced to one-third or less.

The only conclusions to be drawn from these and other experiments are that castelamarin is a substance of low toxicity and of only slight pharmacological activity.

The author wishes to thank Prof. George Barger, F.R.S., for his interest in these investigations, and Prof. J. W. Gunn of Capetown University for allowing him the use of the pharmacological laboratory.

DEPARTMENT OF PHYSIOLOGY,
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[Received, October 24th, 1922.]

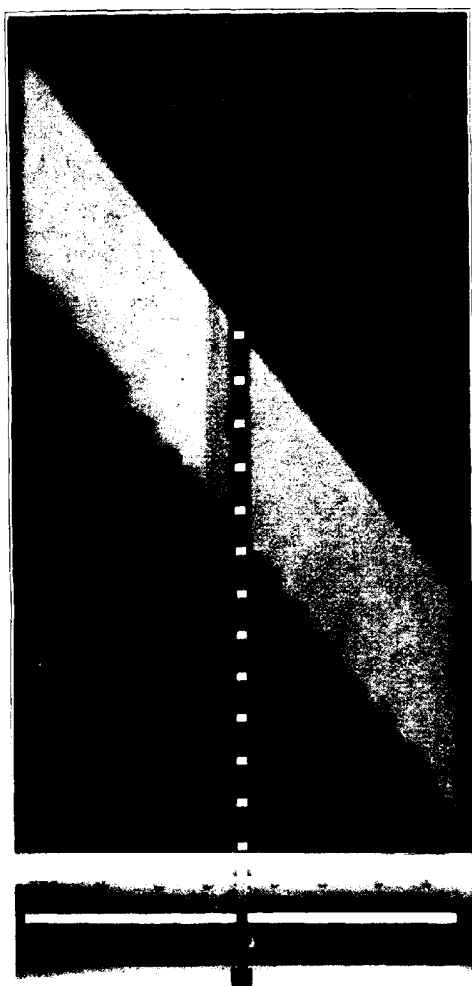
XXVI.—*The Speed of the Uniform Movement of Flame in Mixtures of the Paraffins with Air.*

By WALTER MASON.

THE series of determinations recorded in the present paper, on the speed of the "uniform movement" of flame in mixtures of methane, ethane, propane, butane, and pentane, respectively, with air, were made at the request of Professor Wheeler, who required accurate information as to the composition of the mixtures of each hydrocarbon with air which would yield the maximum speed of uniform movement of flame under standard conditions of experiment. Similar determinations had been made by Payman (T., 1919, 115, 1446), using the so-called "screen-wire" method of recording flame velocities; it was desired to check these results by means of the more accurate photographic method. Each method is trustworthy, and the former is sufficiently accurate for most purposes, being at the same time easier to employ, in many instances, than the photographic method. The photographic method enables an accurate analysis to be made of the behaviour of the flame and is an extension of that devised by Mallard and Le Chatelier, who photographed the movements of such flames as possessed a high actinic value on a sheet of gelatino-bromide paper wrapped round a rapidly revolving drum. For the extension of the method to enable flames of low actinic value to be photographed, a brass tube was constructed holding a window or slit of quartz, 30 cm. long, and a quartz lens was employed to focus the slit on a rapidly revolving sensitised film.

The tube, a portion of which is shown at the foot of Fig. 1, is 5 cm. in diameter, and it is divided up accurately into sections of various lengths which can be joined together, forming a total length of 2.4 m. Two 20 cm. lengths each hold a quartz strip, 15.5 cm. long, 1.5 cm. wide, and 3 mm. thick, which covers an aperture, 15 cm. long and 1 cm. wide, cut in the section. The end of each section of the tube is flanged, and fitted with an interchangeable spigotted joint, which ensures a uniform surface. Each

FIG. 1.



flange is carefully faced, so as to form a perfectly gas-tight joint, when slightly greased, with the flanged surface of any other section, and the sections can be secured together by size 10 B.A. nuts and bolts, six to each joint.

The two sections holding the quartz windows when bolted together form a section 40 cm. long, having a window 30 cm. long and 1 cm. wide divided at the centre by the flange joint 1 cm. wide. This division throws a shadow on the film, which, when the film is moving, is reproduced as a black line and forms a convenient base for the measurement of the angle produced by the combined effects of the horizontal movement of the flame and the vertical movement of the film. The method of providing an open end to the tube (as required when the uniform movement of flame is to be measured) is similar to that described in a previous communication (T., 1914, **105**, 2410); a brass plate, holding a tubulure for the admission of the mixture, and forming when greased a gas-tight joint with the flange of any section, can be gently slid to one side just before ignition. It will be apparent that the interchangeability of the various sections enables photographs to be taken of any stage of the progress of the flame (over a distance of 30 cm.) at any desired situation along the tube; so that, by using a mixture of constant composition and maintaining a constant length of tube, a succession of photographs can be obtained which, when placed together, will reproduce the manner of propagation of flame throughout the whole tube. By these means Mason and Wheeler obtained the photographs reproduced in T., 1920, **117**, 46, Plate I.

The camera used for photographing the flames consists of a light-tight box furnished with a quartz lens, and containing a drum for the reception of the film, which can be revolved at any desired speed. The focal length of the lens is 17 cm., its diameter being 13 cm., and its position is so fixed in the camera that the size of the image obtained on the film is one-quarter that of the object. The drum takes a length of 47 cm. of film and is 10 cm. wide. Its spindle projects through light-tight bearings on each side of the camera, and carries at one end a pulley to receive the drive of an electric motor.

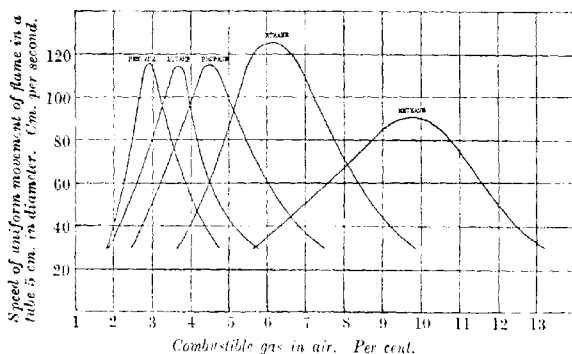
The method of timing the rate of revolution of the film is to allow the sparks which occur at the mercury break of an electrically operated tuning-fork (50 vibrations per second) to focus themselves through a slit in the back of the camera, on the moving film, so that they fall on the shadow cast by the 1 cm. flange which separates the quartz windows in the explosion tube (see Fig. 1).

The Uniform Movement of Flame in Mixtures of the Paraffins with Air.

Using the brass tube and the camera as described, the speeds recorded in Table I were obtained. The sections of the tube containing the windows were the first two sections, and the tube was 2 m. long. The flame was photographed after it had travelled 5 cm. from the open end, where the mixtures were ignited by a diaphragm of flame passed across it.

The results are shown diagrammatically, as speed-percentage curves, in Fig. 2, and a reproduction of one of the photographs is given in Fig. 1 (ethane, 6.05 per cent.).

FIG. 2.



The speeds of the uniform movement of flame in this series of mixtures were determined by Payman (*loc. cit.*), using a glass tube 2.5 cm. in diameter, by the screen-wire method. The figures recorded by him for the mixtures in which the speed of flame was fastest are given in the table that follows (Table II), for comparison with those obtained in the present research.

The differences are not very great, although for the particular purpose for which the results were required they are of importance. It will be realised that the photographic method is more accurate than the screen-wire method, if only for the reason that one can rest assured that only the "uniform movement" has been included in the calculations of speeds, and not, as sometimes may occur with the screen-wire method, part of the "vibratory movement" also. Nevertheless, the last-named method is very useful, and there are already on record a number of determinations for different inflammable gases obtained by its means and directly comparable because

TABLE I.

Speed of uniform movement of flame in mixtures of the paraffin hydrocarbons with air in a horizontal brass tube 5 cm. in diameter.

Methane.		Ethane.		Propane.	
Per cent. in air.	Speed in cm. per sec.	Per cent. in air.	Speed in cm. per sec.	Per cent. in air.	Speed in cm. per sec.
5.95	34	3.45	6 *	2.90	45
6.33	40	4.36	55	3.66	89
7.03	49	5.15	88	4.21	110
8.12	66	5.46	116	4.47	114
9.00	84	5.84	125	4.50	114
9.53	91	6.05	127	4.90	106
10.12	90	6.32	125	5.29	99
10.64	84	6.72	117	5.80	64
11.44	64	7.20	107	7.15	34
12.7	35	7.71	81		
13.3	23	9.00	42		
		10.07	31		

Butane.		Pentane.	
Per cent. in air.	Speed in cm. per sec.	Per cent. in air.	Speed in cm. per sec.
1.91	30	1.59	17 *
2.25	48	2.35	56
2.93	69	2.55	90
3.38	99	2.87	115
3.56	113	3.15	107
3.73	112	3.44	91
4.27	75	3.58	70
5.13	40	4.32	41
5.91	28		

* These mixtures did not allow flame to propagate throughout the tube.

TABLE II.

Mixtures in which speed of uniform movement of flame is fastest.

Gas.	Per cent. in air.	
	As determined photographically.	As determined by screen-wire method (Payman).
Methane	9.65	9.50
Ethane	6.05	6.50
Propane	4.45	4.70
Butane	3.65	3.65
Pentane	2.90	3.00

made under identical conditions in a glass tube 2.5 cm. in diameter. All the determinations were made in this laboratory. They are: hydrogen (Haward and Otagawa, T., 1916, **109**, 85); methane (Mason and Wheeler, T., 1917, **111**, 1044); acetylene (Mason and

Wheeler, T., 1919, **115**, 578); carbon monoxide, ethane, propane, butane, and pentane (Payman, T., 1919, **115**, 1452); and ethylene (Chapman, T., 1921, **119**, 1677).

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XXVII.—*The System Tin-Arsenic.*

By QASIM ALI MANSURI.

SEVERAL compounds of tin and arsenic are described in chemical literature. Spring (*Ber.*, 1883, **16**, 324), by submitting tin and arsenic to high pressure, obtained a substance to which he gave the formula Sn_3As_4 . Headden (*Amer. J. Sci.*, 1898, [iv], **5**, 95; *Proc. Colorado Sci. Soc.*, 1901, **6**, 80) described some crystals, obtained from a Cornish tin mine, of a tin arsenide, to which he gave the formula Sn_6As ; he commented on the difficulty of separating these crystals from globules of tin. Stevanovic (*Z. Kryst. Min.*, 1905, **11**, 326) measured Headden's crystals and found that the angles of crystals of the arsenide Sn_3As_2 lie between the corresponding values for the arsenide Sn_6As and arsenic. Groth ("Chemische Krystallographie," 1906, I, 66) corrected his erroneous chemical formula.

Stead (*J. Soc. Chem. Ind.*, 1897, **16**, 200) found that tin at about 800° alloyed with as much as 43 per cent. of arsenic, but on prolonged heating at higher temperatures much of the arsenic was volatilised. He also made a micrographic study of the alloys. In the alloys containing between 0.05 per cent. and 10 per cent. of arsenic, hard plates appear in the polished sections as straight white lines, which are really sections of flat plates. When an alloy containing 99.5 per cent. of tin and 0.5 per cent. of arsenic is cooled very slowly, crystals are concentrated in the upper layers, and below is the parent-substance practically free from these crystals. The crystals of an arsenide of tin, thus separated, were examined microscopically. They were quite large and therefore some of their physical properties could be easily studied. It does not appear from Stead's work that thermal results of much importance were obtained. It is mentioned, however, that the melting point of the separated parent substance was 232° , and that the final thermal arrest during solidification of the alloys containing, respectively, 5, 10, and 20 per cent. of arsenic was also 232° , which is identical with the melting point of pure tin. Thus the parent substance was shown to be pure tin and not a eutectic of tin and

arsenic. Several crops of crystals of the arsenide were prepared and analysed, with results which indicated the formula Sn_3As_2 .

Jolibois and Dupuis (*Compt. rend.*, 1911, **152**, 1312) seem to have made the first systematic thermal study of the system up to about 50 per cent. of arsenic. They report the existence of two compounds, Sn_4As_3 and SnAs . The thermal results obtained, however, are not very trustworthy.

According to the thermal investigation made by Parravano and de Cesaris (*Rend. R. Accad. Lincei*, 1911, [v], **20**, 593; *Gazzetta*, 1912, **42**, i, 274) the melting point of tin is raised by the addition of arsenic, and the curve of the melting points of the alloys rises, at first steeply and then more slowly, to the limit reached in the experiment. Their curve is more or less a continuous one and has no breaks or sharp maxima. Three horizontals are found in the diagram. The first, at a temperature corresponding with the melting point of tin, runs from pure tin to an alloy containing about 30 per cent. of arsenic. The second runs from that alloy to another containing about 40 per cent. of arsenic, and the third is between the 40 and 50 per cent. alloys. Parravano and de Cesaris have inferred from these three horizontals the existence of the compounds Sn_3As_2 and SnAs . The region of existence of the compound SnAs is somewhat restricted and the compound is dissociated on fusion.

The work mentioned above appears to be all that has been published on this subject. There is no doubt that the study of a system containing arsenic is quite an intricate one and many experimental difficulties have to be faced, partly because many of the properties of the element itself have not been satisfactorily investigated (even the melting point of arsenic is not known with certainty and there is very little information available about its different allotropic forms) and partly because in ordinary circumstances arsenic passes from the solid to the gaseous state at about 450° (Roscoe and Schorlemmer, "A Treatise on Chemistry," 1905, I, 673). Thus, owing to the volatile nature of arsenic, it becomes very difficult to work with it at higher temperatures. Most of the systems containing arsenic have therefore been studied up to about 50 per cent. of arsenic only.

The author has made a complete study of the system tin-arsenic from pure tin to practically pure arsenic, and his diagram is the first complete one of an arsenic system. The investigation has satisfactorily and completely solved the problem of the interaction of tin and arsenic and verified work previously done, and it is hoped that it will remove the doubts of chemists and metallurgists as regards any other possible compounds of the two elements.

EXPERIMENTAL.

Preparation of Alloys.—The alloys were prepared in Ullmann tubes as has been fully explained in the author's paper on the system thallium-arsenic, presented at the 1922 autumn meeting of the Institute of Metals.

Very pure tin and doubly sublimed arsenic were used. The quantity of alloy that could be prepared in one operation did not exceed 20 to 30 grams, as the coarsely powdered arsenic occupied much space, and the unusually long tube thereby rendered necessary

FIG. 2.

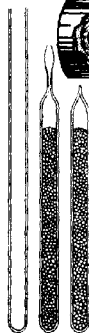


FIG. 1.

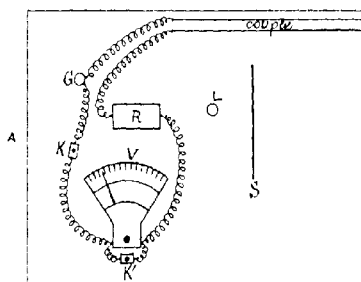


FIG. 3.

Showing the method of taking cooling curves.

FIG. 1.—Preparation of the glass tubes in which the alloys were heated.

FIG. 2.—Heating arrangement.

FIG. 3.—Recording arrangement. A = galvanometer. V = millivoltmeter. R = resistance. K and K' = keys. L = light. S = water-drop curve-tracer screen.

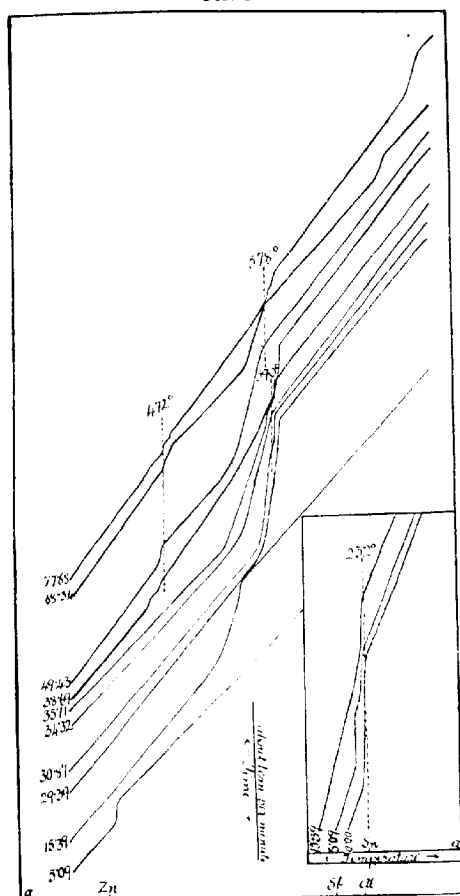
was liable to crack. Thus, at the arsenic end of the series, only 20 grams of the alloys could be prepared, but at the tin end 30 grams were manipulated.

Thermal Analysis.

Haskin's chrome-nickel and constantan couple (Burgess and Le Chatelier, "Measurement of High Temperatures," 1912, p. 170) was used throughout this investigation for the reasons mentioned in a previous paper (T., 1922, 121, 2272). The hot junction was applied in close contact outside the glass tubes in which the alloys were prepared. The cooling curves were obtained in the same

way as explained in the paper on the system thallium-arsenic (*loc. cit.*). The apparatus is shown in Figs. 1, 2, and 3. The curves

FIG. 4.

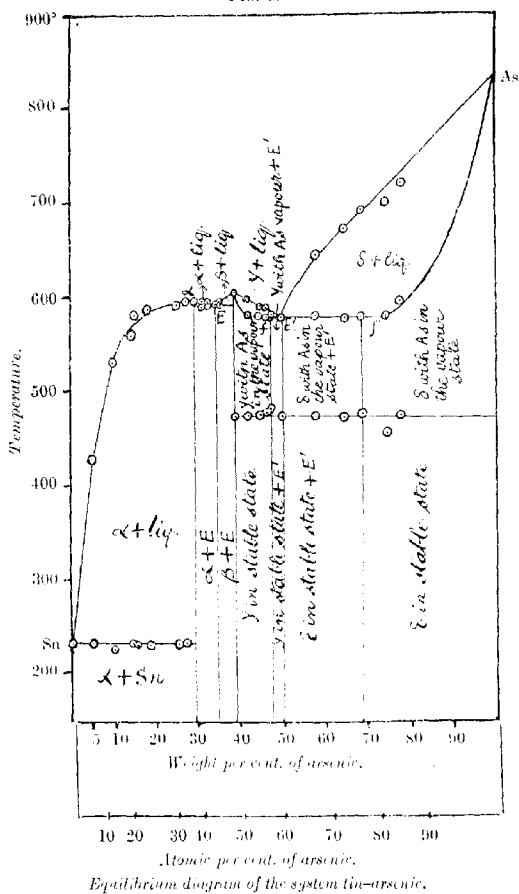


Some typical cooling-curves of tin-arsenic alloys as obtained on the water-drop curve-tracer. (Reduced by about 60 per cent.) The tin end has been shifted to the right. The figures on the left of the curves represent weight per cent. of arsenic in the alloys.

thus obtained are given in Fig. 4, from which it is clear that the thermal changes are quite real. To safeguard against any extra

points appearing on the curves, which might be due to other causes, curves of pure tin and of pure arsenic were taken in exactly the

FIG. 5.



same circumstances. From these data the equilibrium diagram of the system tin-arsenic was plotted as given in Fig. 5.

Alloys containing more than 80 per cent. of arsenic melt at temperatures so high that the glass tubes begin to soften and the

arsenic is blown out; therefore no direct analysis of these high-percentage arsenic alloys could be made. This portion of the curve was, however, studied by heating the mixtures of arsenic and tin to different high temperatures and noting the minimum temperatures at which a uniform alloy was formed. This gave the position of the *liquidus*; the position of the *solidus* was determined by chilling the alloys.

Alloys for this investigation were prepared in sealed glass tubes in the same way as other alloys, but a cap was screwed to the iron tube in which the glass tube was packed, so that arsenic could not be blown out on account of the tightly packed sand. A couple could not be attached to the glass tubes without destroying the efficiency of the packing.

Chilling.—Except in the case of a few alloys of very low melting point, all alloys to be chilled were sealed in glass tubes, which were packed in sand in iron tubes, and heated to a temperature a little higher than the melting point of the alloy. They were then cooled very slowly to the temperature at which chilling was required, the containing iron tubes were kept at that temperature for fifteen to twenty minutes, and then quickly dipped in a bucket of cold water.

This method of chilling is not very satisfactory, as the sand does not lose heat sufficiently quickly. But the alloys could not be heated in any other way without losing a considerable quantity of arsenic.

Result of the Thermal Analysis.

Percentage of arsenic.	Critical points observed in degrees centigrade.		Percentage of arsenic.	Critical points observed in degrees centigrade.	
nil *		232	38.69 *	605	472
5.09	428	231.5	41.72	596	472
9.93	529	225	44.57	590	474
14.55	557	232	46.08	587	474
15.39	579	231.5	47.06	579	476
18.31	586	230	49.43 *	578	471
25.28	589	231.5	49.36 *	579	468
26.91	595	232	57.63	644	472
29.39 *	596		64.37	672	472
30.87	595	590	68.34	692	475.5
32.43	595	589	74.32	700	455
34.32 *	591		77.68	720	473
35.11	595	591			

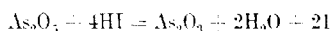
Alloys marked * froze at a single temperature. Alloys containing 85, 90, 95, and 100 per cent. of arsenic, chilled at 750°, 778°, 809°, and 850°, respectively, were completely molten.

Chemical Analysis.

About half a millimetre of the surface of the alloy was filed off to remove oxides and impurities, if there were any. One to two

grams of the finely powdered alloy were treated with 30 c.c. of nitric acid (*d* 1.4) and 15 c.c. of water. Alloys containing up to about 30 per cent. of arsenic dissolved easily in this medium on warming, but alloys containing a higher percentage of arsenic were brought completely into solution only after heating with nitric acid (*d* 1.4) for several days. The greater part of the acid was removed by evaporation, some metastannic acid separating, and to the cooled residue 5 to 10 c.c. of aqueous ammonia were added, care being taken that the solution remained acid. The solution was then diluted with about 200 c.c. of water, well shaken, and left over-night. In this way, in the presence of nitric acid and ammonium nitrate, tin is precipitated completely if the solution is not very concentrated. The precipitate was collected, well washed with warm water, and weighed as SnO_2 . Prolonged washing of the precipitate is necessary for complete removal of arsenic acid. The filtrate and washings were evaporated, cooled, and made up to 500 c.c. Twenty-five c.c. of this solution were neutralised with sodium hydroxide, 25 c.c. of strong hydrochloric acid added, the mixture was well cooled, and, 3 grams of potassium iodide having been added, the liberated iodine was titrated with standard sodium thiosulphate.

According to Williamson, the action



takes place in the presence of an excess of hydrochloric acid in the cold.

Results of Analysis.

Per. centage of tin.	Per. centage of arsenic.	Average per. centage of arsenic.	Error in 100.	Per. centage of tin.	Per. centage of arsenic.	Average per. centage of arsenic.	Error in 100.
99.94	nil.	nil.	— 0.06	54.01	46.16	46.08	+ 0.09
95.07	5.25	5.09	— 0.16	52.59	46.71	47.06	— 0.35
89.85	9.71	9.93	— 0.23	50.45	49.31	49.43	— 0.12
85.46	14.54	14.55	— 0.08	50.20	48.92	49.36	— 0.44
84.45	15.22	15.39	— 0.12	* 42.50	57.77	57.63	— 0.13
81.62	18.23	18.31	— 0.07	42.56	57.81	57.62	+ 0.18
74.61	25.17	25.28	— 0.11	35.68	64.42	64.37	— 0.05
73.00	26.82	26.91	— 0.09	* 31.69	68.38	68.34	— 0.07
70.67	29.45	29.39	— 0.06	31.92	67.70	67.89	— 0.19
69.18	30.92	30.87	— 0.05	25.60	74.23	74.32	— 0.08
67.69	32.55	32.43	— 0.12	22.56	77.93	77.68	+ 0.24
65.66	34.29	34.32	— 0.08	15	85	†	
64.38	35.01	35.11	— 0.51	10	90	†	
61.21	38.60	38.69	— 0.10	5	95	†	
58.10	41.54	41.72	— 0.18	nil.	99.82	99.82	— 0.18
55.34	44.45	44.57	— 0.09				

* Duplicates.

† These alloys did not give constant results owing to their not being of a uniform nature.

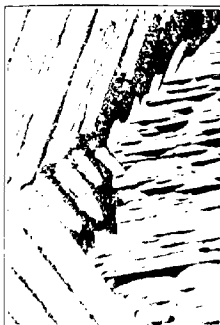
FIG. 6



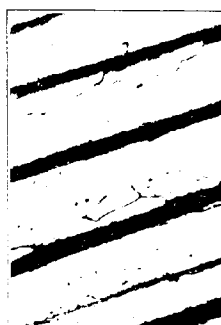
(a) 52.5% As, showing sections of the plates of a as white lines and tin as dark. This is the typical structure of the alloys at the tin end of the series. As the percentage of arsenic increases, the white lines become more numerous and the dark tin decreases. Magn. 30.



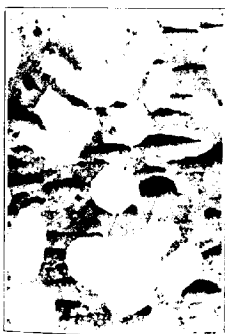
(b) 14.5% As, annealed at 580°C, showing complete solubility of a in tin at 580°C. Magn. 30.



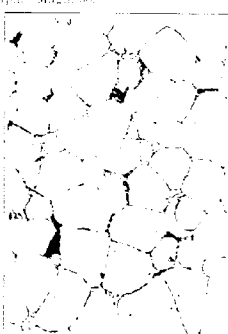
(c) 25.2% As, showing dark tin separating out between layers of a. As the plates of a of arsenic increases, the dark portion becomes less and less until at 29.3% As the uniform structure of a only is seen as broad white bands. Magn. 30.



(d) 32.4% As, showing plates of a with a bent interface between the tin. At 37.0% As, the pure a solubility structure is seen as alternating and very narrow white and dark lines. This structure was very difficult to photograph. Magn. 30.



(e) 50.1% As, showing a and a solubility structure. Magn. 30.



(f) 85.6% As, showing a and a solubility structure. Magn. 30.

All of the above are in the series of alloys of a and tin.

FIG. 7.



(a) 41.72% As, showing solid solutions γ . Magn. 50.



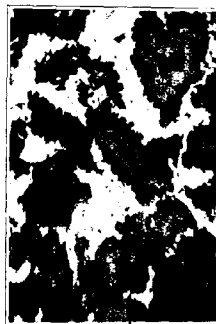
(b) 47.06% As, showing white crystals of β As-antecite. Magn. 50.



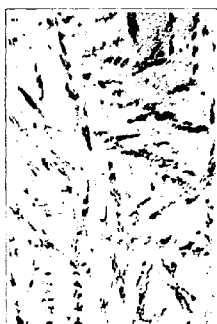
(c) 49.36% As, showing the uniform structure of β -As-antecite. Magn. 50.



(d) 64.37% As, showing dark crystals of β As-antecite. Magn. 50.



(e) 68.74% As, showing small crystals of β with a little β -As-antecite. The colored portion indicates the percentage of arsenic there was added to the Fe-As alloy. These alloys are difficult to photograph, owing to slow reduction of Fe. Magn. 50.



(f) 68.74% As, cooled at 600, showing small crystals of β with a little β -As-antecite. Magn. 50.

With each sample of hydrochloric acid used, a blank experiment had to be performed, as strong hydrochloric acid also acts on potassium iodide and sets free iodine.

With a little practice, the proper strength of the sodium thiosulphate solution which should be used with the arsenic acid solution of a given strength can be ascertained, and then the method is trustworthy. The strengths of both solutions should be as nearly equal as possible, a stronger thiosulphate giving low results and a weaker thiosulphate high results.

Micrographic Analysis.

With the exception of a few alloys containing much free tin, because of a certain amount of flow in them, and a few alloys containing much free arsenic, owing to their being very brittle and of a spongy nature, all the alloys were quite easily polished. A suitable piece was cut and roughly flattened on an old, blunt file. It was smoothed on a coarse emery paper and then rubbed successively on the French blue emery papers 0, 00, and 000. These emery papers, after being used for some time, produce better results than when they are new. A very good surface could sometimes be obtained with an old 000 paper alone. But in most cases the final polish was given by diamantine powder, used wet on a revolving pad.

The surface was then etched with very dilute ferric chloride and a trace of hydrochloric acid or with bromine water. In a few cases, copper ammonium chloride and hydrochloric acid were also used.

In alloys showing free tin, the latter was darkened while the other constituent remained bright. Other alloys, containing high percentages of arsenic, were very difficult to etch with the ferric chloride reagent; however, after action lasting about two hours, the α - β and β -As eutectics and the solid solution δ were also darkened. These alloys were etched better with bromine water, which had the same effect of darkening the α - β and β -As eutectics and δ .

The photomicrographs given in Figs. 6 and 7 illustrate the structure of the different alloys.

Conclusion.

This work clearly establishes that:

1. Tin and arsenic alloy in all proportions.
2. These elements form only two compounds, Sn_3As_2 and SnAs , as proved by two distinct maxima in the curve of thermal equilibrium, by chemical analysis, and by the photomicrographs.

3. The melting point of arsenic lies between 800° and 850° , but arsenic, once molten, supercools considerably, like antimony, before it begins to solidify again.

4. The melting point of tin is practically not lowered by the addition of arsenic. At the tin end of the series, all the arsenic added seems to combine with tin and form the compound α , which dissolves in molten tin.

At the concentration of 29.5 per cent. of arsenic, the alloy freezes at a single temperature and is the compound α itself.

The rest of the system up to an alloy containing about 39 per cent. of arsenic is of the usual eutectiferous type. At that composition, the second compound of tin with arsenic— SnAs_2 —is formed. This compound forms a partly eutectiferous system with arsenic, with the formation of the solid solutions, γ and δ , at both ends respectively.* The arsenic contained in these solid solutions is probably in the vaporous state above about 472° , and they are, so to speak, in a dissociated state; below that temperature, the alloy solidifies and the solid solutions assume the stable form. These alloys, chilled below 472° , have a uniform structure similar to that shown in Fig. 7*d*, but when chilled just above 472° they are porous, like sponge.

It is these solid solutions that have arsenic vapour present as one of their constituents and therefore it is they that are in a dissociated state, so to speak, and not β , as suggested by Parravano and de Cesaris. All alloys containing these solid solutions give a thermal arrest at 472° . What those authors were dealing with was the solid solution, γ , just near the composition of β . The composition of the β prepared by the author was 38.69 per cent. of arsenic and the remainder tin, instead of the theoretical percentage, 38.66, of arsenic. Even this slightly impure β gave a distinct thermal arrest at 472° , due to the vapour of arsenic, present in γ , solidifying at that temperature.

5. A point of great practical interest which has been revealed by the study of this system is that the alloys of tin with arsenic are very similar to those of tin with phosphorus (*J. Institute Metals*, 1920, 23, 325) in most of their properties and in their crystalline structure. The thermal curve of the Sn-P system is very similar to that of the Sn-As system, and the photomicrographs of one system compare very well indeed with those of the other. The

* It is interesting to note that at the eutectic limits, f and f' , the composition of the alloys is about 47 per cent. and 70 per cent. of arsenic, respectively, and thus they may be considered as the highly dissociated compounds Sn_2As_3 and SnAs_4 , respectively (Sn_2As_3 requires $\text{As} = 48.60$, SnAs_4 requires $\text{As} = 71.40$ per cent.).

physical properties agree quite well, in accordance with the similarities of the temperature-concentration curves and of micro-structure.

Again, the two systems, Cu-P (*Z. anorg. Chem.*, 1907, **52**, 131) and Cu-As (*J. Institute Metals*, 1910, **3**, 34), are also similar. It has also been noted that arsenic has no very injurious effect on copper (*ibid.*, 1913, **10**, 275). On account of the similarity of the two systems it should be possible to make arsenical bronzes having properties similar to those of phosphor-bronzes.

There is only one other point to be discussed, and that is the effect of pressure. The system was studied with the aid of alloys prepared in sealed glass tubes, in which the pressure could not remain constant. The glass tubes in which the alloys were prepared were exhausted to a pressure of about 15 mm., and therefore the pressure in them would be less than one atmosphere ("Physikalische Chemie Tabellen," 1912, p. 375) up to about 600°, which is the melting point of the compound SnAs. Above that temperature, the pressure may become greater than one atmosphere.

Now it remains to see what effect this variation of pressure should have on the system Sn-Sn₃As₂ and the eutectiferous system Sn₃As₂-SnAs. As a reduction of pressure of about one atmosphere has practically no effect on the melting point of metals, these systems should not be affected by such a change of pressure. Only the eutectiferous system β -As should be affected, in so far that at higher pressures more arsenic vapour must dissolve in β , and thus γ and δ , richer in arsenic, will be formed. The question, however, is what difference will a change of pressure of about half an atmosphere cause in the composition of γ and δ and therefore in their properties. The change will actually be so small that the properties of γ and δ will remain practically the same throughout and the system β -As will also remain unaffected by the slight changes of pressure. The equilibrium diagram of the system tin-arsenic worked out by the author therefore represents the true equilibrium of the system.

The author had the privilege of working at this problem in the Goldsmiths' Research Laboratories of the Cambridge University. He is very much indebted to Mr. C. T. Heycock for his sympathetic guidance and advice throughout the work.

[Received, October 2nd, 1922.]

XXVIII.—*peri-Naphthindigotin*.

By SIKHIBHUSHAN DUTT.

ALTHOUGH the analogous thioindigotin has been prepared (Meister, Lucius, and Brüning, D.R.-P. 198050), *peri-naphthindigotin* has not hitherto been made. Wichelhaus (*Ber.*, 1893, **26**, 2547) obtained α - and β -naphthindigotins from the corresponding naphthylglycines by fusion with potassium hydroxide, and subsequently, by employing Blank's method (*Ber.*, 1898, **31**, 1812), he improved the yield (*Ber.*, 1899, **32**, 1236). The Badische modification of the Heumann synthesis has been applied by Fierz and Tobler (*Helv. Chim. Acta*, 1922, **5**, 537) to the preparation of β -naphthindigotin, but Fierz and Sallmann's attempts to prepare *peri-naphthindigotin* were unsuccessful (*ibid.*, p. 560).

This substance has now been prepared, although in very poor yield, from naphthastyril by the modified Heumann process. The naphthastyril was prepared by Pisovschi's method (*Bull. Soc. chim.*, 1911, **9**, 86), and although he claims a quantitative yield, the present author could not obtain more than 50 per cent. of the theoretical quantity.

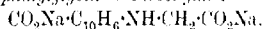
peri-Naphthindigotin closely resembles the α - and β -isomerides in physical and chemical properties. However, the lightness and the fugitive character of the shade which it produces on the fibre, together with its extremely poor yield, render this substance valueless technically.

EXPERIMENTAL.

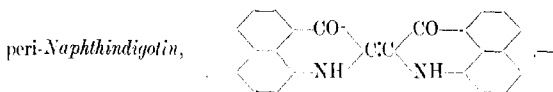
Naphthastyrilacetic Acid, $C_{10}H_6 \begin{smallmatrix} \diagup CO \\ \diagdown NH \cdot CH_2 \cdot CO_2H \end{smallmatrix}$.—A solution of

8 grams of naphthastyril in 100 c.c. of 10 per cent. potassium hydroxide was treated with 5 grams of chloroacetic acid. The mixture was warmed for about five minutes, hydrochloric acid added, and the white precipitate crystallised from alcohol: m. p. 258° (Fierz and Sallmann, *loc. cit.*, give 256°) (Found: C = 68.1; H = 4.4. Calc., C = 68.4; H = 4.3 per cent.).

Disodium α -Naphthylglycine-8-carboxylate.



—The solution of the sodium salt prepared from 11 grams of naphthastyrilacetic acid, 4.4 grams of sodium hydroxide, and 15 c.c. of water was poured into about 150 c.c. of absolute alcohol, when the disodium salt, already described by Fierz and Sallmann (*loc. cit.*), was precipitated as a white powder with fatty lustre.



Twelve grams of the above disodium salt having been slowly added to a mixture of 40 grams of dry sodium hydroxide and 20 grams of sodamide maintained at 260°, the temperature was gradually raised to 280°, kept at this point until frothing ceased, and then rapidly raised to 300°. The mass was kept at this temperature for one minute, cooled, and boiled with water containing sodium hyposulphite. The filtered solution, after extraction with ether, was treated with aqueous potassium ferricyanide. The precipitate, which weighed only 0.7 gram after washing and drying, was a dark blue, almost black substance, only sparingly soluble in aniline, nitrobenzene, or quinoline. It could be obtained only in crystalline aggregates, not in definite crystalline form, from any of these solvents. It dissolves in alkaline hyposulphite with a reddish-brown colour, and dyes wool and cotton in light green shades which are rather fugitive to light. When strongly heated, the substance decomposes with evolution of a reddish-brown vapour. It dissolves in strong sulphuric acid with a bluish-green colour, and when rubbed between hard surfaces it acquires a copper-coloured, metallic lustre (Found: C = 78.5; H = 3.9; N = 7.3. $C_{24}H_{14}O_2N_2$ requires C = 79.55; H = 3.8; N = 7.7 per cent.).

The author expresses his best thanks to Mr. Satyendra Nath Bose for his kind encouragement during the progress of the work.

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[Received, November 27th, 1922.]

XXIX.—Dyes derived from Diphenic Anhydride.

By SIKHIBHUSAN DUTT.

DIPHENIC anhydride, which has properties very similar to those of phthalic anhydride, has not hitherto been condensed with amino- or hydroxy-compounds, with a view to obtain colouring matters analogous to the phthaleins. This observation together with the fact that diphenic anhydride contains a seven-membered ring led the author to undertake the present investigation, with the hope that such condensation products would possess interesting tinctorial and fluorescent properties, similar to those of the substances obtained from six-membered dibasic acid anhydrides like naphthalic

anhydride (Terrisse, *Annalen*, 1885, **227**, 1102; Graebe and Aubin, *ibid.*, 1888, **247**, 286; Jaubert, *Ber.*, 1893, **26**, 992), or camphoric anhydride (Sircar and Dutt, T., 1922, **121**, 1283).

Methods suitable to the purpose have been worked out and diphenic anhydride has been condensed with phenol, resorcinol, *m*-dimethylaminophenol, and phloroglucinol. The condensation product with resorcinol has been brominated and a tetrabromo-compound obtained.

In comparison with the corresponding phthaleins it is found that although the fluorescence in these compounds is only slightly weakened, the tinctorial properties are considerably diminished. In fact they yield such light and fugitive shades on wool that they are quite valueless as dyestuffs.

EXPERIMENTAL.

Phenoldiphenic, $\begin{matrix} \text{C}_{12}\text{H}_8 \\ \text{CO-O} \end{matrix} > \text{C}(\text{C}_6\text{H}_4\cdot\text{OH})_2$.—A mixture of 8 grams of

diphenic anhydride, 16 grams of phenol, and 12 grams of stannic chloride was heated at 120–130° for sixteen hours. Excess of phenol was distilled off in steam, and the residue, having been extracted with sodium bicarbonate solution to remove diphenic acid, was dissolved in dilute ammonia, and the filtered solution acidified with hydrochloric acid. The precipitate crystallised from dilute alcohol in pinkish-white needles containing two molecules of water of crystallisation. It shrinks at 100°, and melts at 131° with evolution of carbon dioxide.

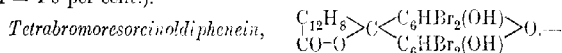
The substance is very soluble in organic solvents, and dissolves in sodium hydroxide solution with a reddish-pink colour (Found: C = 72.5, 72.6; H = 4.7, 4.9. $\text{C}_{26}\text{H}_{18}\text{O}_4 \cdot 2\text{H}_2\text{O}$ requires C = 72.6; H = 5.1 per cent.). The *diacetyl* derivative crystallises from alcohol in colourless prisms melting at 142° (Found: C = 75.1; H = 5.0. $\text{C}_{30}\text{H}_{22}\text{O}_6$ requires C = 75.3; H = 4.6 per cent.). The *dibenzoyl* derivative crystallises from light petroleum in colourless needles, m. p. 186–188° (Found: C = 79.2; H = 4.3. $\text{C}_{40}\text{H}_{26}\text{O}_6$ requires C = 79.7; H = 4.3 per cent.).

Resorcinoldiphenic, $\begin{matrix} \text{C}_{12}\text{H}_8 \\ \text{CO-O} \end{matrix} > \begin{matrix} \text{C}_6\text{H}_3(\text{OH}) \\ \text{C}_6\text{H}_3(\text{OH}) \end{matrix} > \text{O}$.—A mixture of

10 grams of diphenic anhydride, 12 grams of resorcinol, and 10 grams of fused zinc chloride was heated at 160–170° for three hours. The cold melt was powdered and boiled with dilute hydrochloric acid to remove zinc chloride, and the product, dissolved in dilute caustic soda, was converted by lead acetate into the lead lake, an alcoholic suspension of which was then decomposed by

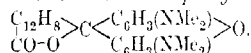
hydrogen sulphide. *Resorcinoldiphenic* was precipitated from the solution with hot water and obtained in brown, glistening prisms, m. p. 172°.

The substance is very soluble in the ordinary organic solvents. It dissolves in caustic alkalis and the yellow solutions show a brilliant green fluorescence (Found: C = 76.1; H = 4.2. $C_{26}H_{16}O_5$ requires C = 76.4; H = 3.9 per cent.). The *diacetyl* derivative crystallises from alcohol in pale yellow needles, m. p. 132° (Found: C = 73.2; H = 4.4. $C_{30}H_{20}O_7$ requires C = 73.1; H = 4.0 per cent.).



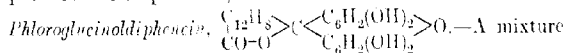
One gram of resorcinoldiphenic, dissolved in 20 c.c. of glacial acetic acid, was treated with 9 c.c. of a 20 per cent. solution of bromine in the same solvent. The mixture was warmed on the water-bath for about ten minutes and poured into water. The product, m. p. 140°, which could not be crystallised, was a pinkish-yellow substance which dissolved in the common organic solvents to give yellow fluorescent solutions. It dissolves in alkali hydroxides with a blood-red colour, but the solution is without fluorescence (Found: Br = 44.6. $C_{26}H_{12}O_5Br_4$ requires Br = 44.2 per cent.).

4:4'-*Tetramethyldiamino-2:2'-oxidodiphenyldiphenic*,



—A mixture of diphenic anhydride (4 grams), dimethyl-*m*-amino-phenol (5.2 grams), and fused zinc chloride (4 grams) was heated at 160–180° for about three hours. The powdered melt was washed with dilute sodium hydroxide and water and boiled with alcohol. The filtered solution, diluted with hot water, deposited the colouring matter in large, pinkish-violet plates, m. p. 128.°

The substance is soluble in a large quantity of dilute hydrochloric acid, forming a pink solution which shows an orange fluorescence. It is also soluble in organic solvents, in which the fluorescence is much stronger (Found: N = 6.6. $C_{30}H_{26}O_3N_2$ requires N = 6.06 per cent.).



of 4 grams of diphenic anhydride, 5 grams of phloroglucinol, and 4 grams of fused zinc chloride was heated at 160–170° for about two hours. The substance, purified through the lead lake, crystallises from alcohol in yellow, microscopic needles, which do not melt below 280°. It dissolves in alkali hydroxides with a blood-red colour, but the solution is without fluorescence. It is fairly soluble

in the common organic solvents (Found: C = 71.1; H = 4.0. $C_{26}H_{16}O_7$ requires C = 70.9; H = 3.6 per cent.).

In conclusion, the author begs to express his best thanks to Mr. Satyendra Nath Bose for the kind interest he has taken in the work.

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[Received, November 27th, 1922.]

XXX.—*The Upper Limit of Diazotisability in the Benzene Series. Diazo-derivatives of Mesitylene.*

By GILBERT T. MORGAN and GLYN REES DAVIES.

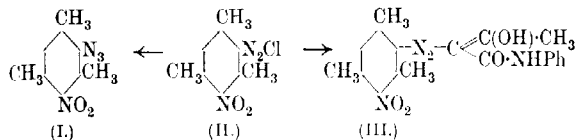
CHEMICAL literature contains innumerable references to the diazotisation of aromatic monamines and diamines, but there is no information available in regard to the degree of diazotisability of monocyclic triamines. For although in their classical study of rosaniline bases E. and O. Fischer prepared trisdiazonium salts, yet in these products each diazo-complex was borne by a separate aromatic nucleus (*Annalen*, 1878, **194**, 269; compare Caro and Wanklyn, *Chem. News*, 1866, **14**, 37). The investigations described below have been directed towards the problem of diazotising to the fullest extent a triamine having all its amino-groups in the same benzene ring in order to ascertain whether the aromatic nucleus can carry at one time more than two diazonium radicles.

In selecting a triamine for this purpose due regard was paid to the factors likely to complicate this diazotising process by the intervention of other reactions such as the formation of aminoazo-compounds, diazoamines, nitroso-derivatives, or internal cyclic diazoimines. The last of these contingencies excludes all bases containing consecutive amino-groups. The formation of aminoazo-compounds or nitroso-derivatives would be avoided by employing a triamine containing no labile hydrogen atoms in ortho- or para-positions with reference to the amino-groups. The tendency to form diazoamines would be lessened by avoiding the use of acidic substituents such as halogens or nitro-groups. A consideration of all the foregoing possibilities of side reactions led us to select triaminomesitylene (XV) as the most suitable base for our experiments. In this triamine each amino-group is in the meta-position with respect to the other two and the intervening ortho-positions are occupied by methyl groups.

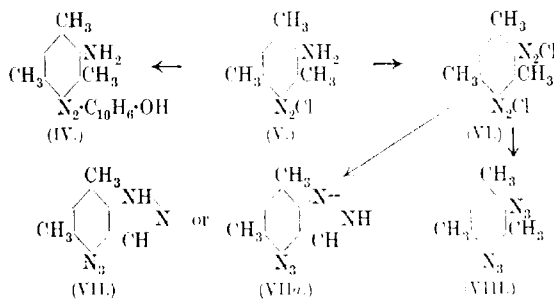
The complete substitution of the benzene ring in triaminomesityl-

one suggests the possibility of steric hindrance, but a preliminary study of other mesitylene bases shows that this factor plays no appreciable part in modifying the course of diazotisation in the mesitylene series. The completely substituted nitrodiaminomesitylene is diazotised with the same readiness as diaminomesitylene and nitromesidine, two bases which each contain one unsubstituted position in the aromatic nucleus.

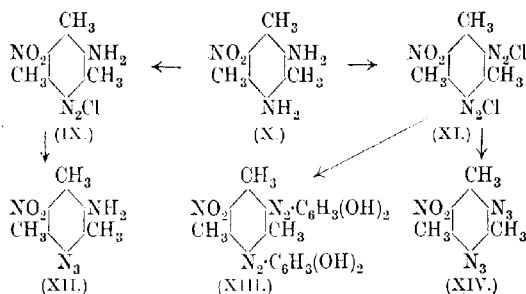
Nitromesidine yields *nitromesitylenediazonium chloride* (II), which is identified by conversion into *chloroaurate* and *dichromate*. These diazonium salts give rise to such well-defined and characteristic derivatives as *nitromesitylene azoimide* (I) and *nitromesityleneazooctoacetanilide* (III).



Diaminomesitylene yields successively monodiazonium and bisdiazonium salts (V and VI), the former identified as its *azo-β-naphthol* (IV) and the latter by conversion into *bis-triazomesitylene* (VIII) and *triazomesityleneindazole* (VII or VIIa). This indazole, which is formed when the diazotisation is carried out with nitrosyl sulphate in strong sulphuric acid, illustrates a tendency often noticeable in bases containing contiguous methyl and amino-radicles.



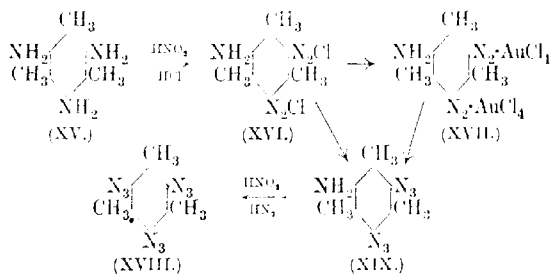
Nitrodiaminomesitylene (X) is readily diazotised in two stages: the monodiazonium and bisdiazonium chloride (IX and XI) being identified by conversion into *nitroaminomesityleneazooimide* (XII) and *nitromesitylenebisazooimide* (XIV), respectively.



The fact that nitrodiaminomesitylene is diazotisable simultaneously in both its amino-groups is proved by coupling with resorcinol after removing excess of nitrous acid with urea; the product is *nitro-mesitylenbisazoresorcinol* (XIII).

Twofold Diazotisation of Triaminomesitylene Hydrochloride.

Diazotisation of triaminomesitylene with nitrosyl sulphate in strong sulphuric acid leads to an indazole derivative and accordingly the process is more smoothly effected in aqueous hydrochloric acid. With a large excess of acid and nitrite, only two of the amino-groups become diazotised and this twofold diazotisation was demonstrated by the isolation of *aminomesitylenbisdiazonium chlorourate* (XVII) and by the formation of *aminomesitylenbisazoimide* (*bistriazomesidine*, XIX). No evidence could be obtained that any three-fold diazotisation had occurred, but after-treatment of the bistriazo-derivative with nitrous acid leads to diazotisation of the remaining amino-group and in the presence of sodium azide the subsequently formed diazonium group is replaceable by a triazo-radicle, giving rise to *tristriazomesitylene* (XVIII). This tristriazo-derivative, which has the remarkable molecular formula $\text{H}_9\text{C}_9\text{N}_9$, is a polymeride of hydrocyanic acid, although apart from the numerical coincidence there is no chemical relationship between the two compounds.



The conclusion to be drawn from the foregoing results is that the benzene ring does not readily carry more than two diazonium groups. The existence of aromatic diazonium salts is certainly connected with the unsaturated character of the aromatic nucleus, and although this unsaturation suffices to give permanence to one or even two diazonium complexes, it is apparently insufficient to confer stability on a third diazonium radicle.

EXPERIMENTAL.

I.—Diazotisation of Nitromesidine.

Dinitromesitylene, obtained by Fittig's method (*Annalen*, 1867, **141**, 134), was partly reduced by Flürsheim's process (*J. Soc. Chem. Ind.*, 1912, **31**, 66. Eng. Pat. 9250 1911): a solution of 6 grams of crystallised sodium sulphide and 0.8 gram of sulphur in 15 c.c. of water was added with mechanical stirring during two hours to 5 grams of dinitromesitylene, suspended in 18 c.c. of boiling water; the mixture was then poured into 20 c.c. of cold water and nitromesidine extracted from the precipitate with dilute hydrochloric acid and obtained as a yellow, crystalline deposit on neutralising the acid extract with ammonia. Nitromesidine (m. p. 73°) was readily and completely diazotised; even the presence of only a slight excess of hydrochloric acid sufficed to prevent the formation of any diazoamino-compound.

Nitromesitylenediazonium Chloroaurate, $\text{NO}_2\text{C}_6\text{H}(\text{CH}_3)_3\text{N}_2\text{AuCl}_4$.—Two grams of nitromesidine, dissolved in alcohol, were diazotised with 2.4 c.c. of concentrated hydrochloric acid and 0.8 gram of sodium nitrite. The cooled, filtered solution was added to a concentrated solution of chloroauric acid, when a pulverulent, greenish-yellow precipitate was formed, oily at first but subsequently becoming solid (Found: Au = 37.04. $\text{C}_9\text{H}_{10}\text{O}_2\text{N}_3\text{Cl}_4\text{Au}$ requires Au = 37.10 per cent.). This chloroaurate was moderately soluble in alcohol and precipitated from solution by water; it intumesced without melting when heated.

Nitromesitylenediazonium Dichromate, $\text{NO}_2\text{C}_6\text{H}(\text{CH}_3)_3\text{N}_2\text{HCr}_2\text{O}_7$.—A bright crocus-yellow precipitate of this salt separated on mixing filtered solutions of nitromesitylenediazonium chloride and sodium dichromate; it turned brown on exposure to light and exploded on gentle warming. When moistened with absolute alcohol and then heated, it decomposed quietly (Found: Cr = 25.32. $\text{C}_9\text{H}_{11}\text{O}_6\text{N}_3\text{Cr}_2$ requires Cr = 25.45 per cent.).

Triazonitromesitylene (Nitromesityleneazoimide) (Formula I).—Sodium azide was added to an acid solution of nitromesitylenediazonium chloride, when a yellow oil separated and solidified on cooling below 0°. This product was collected and purified by

distillation in steam, the distillate was extracted with ether, and crystallised therefrom in colourless needles containing water and melting at 22–23° (Found: C = 25.2. $C_9H_{10}O_2N_4 \cdot H_2O$ requires C = 25.0 per cent.). When crystallised from anhydrous ether, the triazo-compound melted at 23° and contained N = 27.52 ($C_9H_{10}O_2N_4$ requires 27.18 per cent.). This azide was soluble in all organic solvents; it intumescend when heated rapidly and lost two-thirds of its triazo-nitrogen with concentrated sulphuric acid.

Nitromesityleneazob-β-naphthol, $NO_2 \cdot C_6H(CH_3)_3 \cdot N_2 \cdot C_{10}H_6 \cdot OH$, was soluble in glacial acetic acid or in benzene and crystallised from a mixture of the latter and alcohol in tufts of red needles melting at 168° and giving a purple coloration with concentrated sulphuric acid (Found: N = 13.0. $C_{19}H_{17}O_3N_3$ requires N = 12.54 per cent.).

Nitromesityleneazacetacetanilide (Formula III), was obtained by coupling nitromesitylenediazonium chloride and acetoacetanilide (Knorr and Reuter, *Ber.*, 1894, 27, 1169) in alcoholic solution; it separated from benzene, alcohol, or acetone in yellow crystals melting at 171° (Found: C = 61.5; H = 5.77; N = 15.69. $C_{19}H_{20}O_4N_4$ requires C = 61.95; H = 5.44; N = 15.22 per cent.).

Triazomesityleneindazole (Formula VII or VIIa).—Attempts to prepare triazoaminomesitylene by the partial diazotisation of diaminomesitylene have invariably resulted in the production of an indazole derivative, especially when the diazotisation is carried out with chamber crystals. One gram of diaminomesitylene was suspended in 5 c.c. of concentrated sulphuric acid, a few small pieces of ice were added to assist in the solution of the diamine, and 2 grams of chamber crystals were then added followed by more ice until the reaction commenced. When all the chamber crystals had been decomposed, the solution was poured into a mixture of equal volumes of alcohol and ether, giving rise to a white precipitate which soon turned red. This product redissolved in ice-cold water to a dark crimson solution and on adding 1 gram of sodium azide a yellow precipitate was obtained which, unlike the other azides described in this communication, was insoluble in light petroleum, but dissolved in alcohol or benzene. Recrystallised from the latter solvent, it separated in small, yellow needles melting at 134–137° [Found: C = 57.33 (wet process); N = 37.17. *M*, in freezing benzene (*c* = 0.504) = 193, in boiling benzene (*c* = 0.698) = 189. $C_9H_9N_3$ requires C = 57.75; N = 37.4 per cent.: *M* = 187.]

II.—Diazotisation of Diaminomesitylene.

Diaminomesitylene was prepared by reducing dinitromesitylene with tin and hydrochloric acid in aquo-alcoholic solution (Fittig.

loc. cit.). After removing tin compounds and freeing the base with ammonia, the product was purified by repeated crystallisation from light petroleum. The most rapid method of purification was found to be sublimation in a vacuum, when a white, crystalline powder was obtained melting at 90.5°.

A preliminary study of the diazotisation products of diamino-mesitylene (Morgan and Reilly, P., 1914, **30**, 74) had shown that this diamine gave mono- or bis-diazonium salts which had been coupled with β -naphthol. The diamine does not, however, diazotise so smoothly as mesidine or its nitro-derivative. At an intermediate stage (one mol. NaNO_2) its acid solution assumed a red colour and gave neither a stable chloroaurate nor a dichromate. With excess of nitrous acid, the red coloration faded to yellow and the solution gave derivatives of the bisdiazonium salt. This diazotisation proceeds in two stages and unless considerable excess of sodium nitrite is employed the azo-compound produced by coupling with alkaline β -naphthol is a mixture of azo- and disazo-derivatives.

Aminomesityleneazo- β -naphthol (Formula IV).—Two grams of diamino-mesitylene were dissolved in 20 c.c. of 50 per cent. sulphuric acid and diazotised with 1 gram of sodium nitrite; the solution, added to alkaline β -naphthol, gave a crystalline precipitate, which separated from glacial acetic acid and from benzene and petroleum in crimson needles melting at 173° (Found: N = 13.44. $\text{C}_{19}\text{H}_{19}\text{ON}_3$ requires N = 13.77 per cent.).

Mesitylenebisdiazonium Chloroaurate, $(\text{CH}_3)_3\text{C}_6\text{H}(\text{N}_2\cdot\text{AuCl}_4)_2$.—To the yellow solution of the bisdiazonium salt was added a concentrated solution of chloroauric acid, when a light brown, crystalline powder was precipitated, which was slightly soluble in alcohol or acetone (Found: Au = 46.39. $\text{C}_9\text{H}_{10}\text{N}_4\text{Cl}_8\text{Au}_2$ requires Au = 46.24 per cent.).

Mesitylenebisdiazonium Dichromate, $(\text{CH}_3)_3\text{C}_6\text{H}(\text{N}_2\cdot\text{Cr}_2\text{O}_7)_2$, was obtained by adding a concentrated solution of sodium dichromate to the yellow solution obtained by diazotising the diamine in sulphuric acid with a large excess of nitrite. The product is a yellow, crystalline powder darkening in the light and exploding on slight friction (Found: Cr = 26.74. $\text{C}_9\text{H}_{10}\text{O}_7\text{N}_4\text{Cr}_2$ requires Cr = 26.67 per cent.).

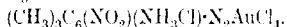
Bis-triazomesitylene (Formula VIII).—To 2 grams of diamino-mesitylene, dissolved in ice-cold dilute alcohol, were added successively 3 grams of sodium azide, 10 c.c. of concentrated hydrochloric acid, and an aqueous solution of 2 grams of sodium nitrite, followed by a further addition of 3 grams of sodium azide. After one hour, the mixture was extracted with ether and the ethereal layer distilled in steam, the distillate being extracted repeatedly with ether. The

etheral extracts were dried over calcium chloride and evaporated, when *bistriazomesitylene* remained as a yellow oil, becoming brown on exposure to air. This bisazide was not so explosive as *m*- or *p*-bistriazobenzene (Forster and Fierz, T., 1907, **91**, 1953; Silberrad and Smart, T., 1906, **89**, 171) and was analysed without difficulty (Found: N = 41.50. $C_9H_{10}N_6$ requires N = 41.58 per cent.). Bistriazomesitylene intumescenced on heating and reacted violently with concentrated sulphuric acid, evolving white fumes; it had a pleasant, fruity odour.

III.—Diazotisation of Nitrodiaminomesitylene.

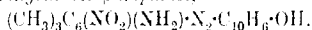
Nitrodiaminomesitylene, formerly obtained by the partial reduction of trinitromesitylene (Fittig, *loc. cit.*), has now been prepared by nitrating diaminomesitylene. An ice-cold mixture of 2.5 c.c. of nitric acid (*d* 1.42) and 2.5 c.c. of concentrated sulphuric acid was added very slowly with stirring to 5 grams of diaminomesitylene, dissolved in 30 c.c. of concentrated sulphuric acid cooled by a freezing mixture. The acid liquid was poured on to 500 grams of ice, and the deep red solution neutralised with ammonia. The brown precipitate was dried and dissolved in benzene, nitrodiaminomesitylene being precipitated by adding light petroleum (b. p. 40–60°). Recrystallisation from benzene or alcohol gave the nitrodiamine in reddish-orange plates melting at 184° (yield 85 per cent. of theory) (Found: N = 21.59. $C_9H_{13}O_2N_3$ requires N = 21.54 per cent.).

Nitroaminomesitylenediazonium Chloroaurate Hydrochloride,



—Nitrodiaminomesitylene (0.5 gram) was dissolved in alcohol and diazotised with 0.18 gram of sodium nitrite and 0.8 c.c. of hydrochloric acid. Carbamide was then added to remove excess of nitrous acid, and the filtered solution treated with chloroauric acid, when the chloroaurate was obtained as a brown precipitate, sparingly soluble in alcohol (Found: Au = 34.13. $C_9H_{12}O_2N_4Cl_5Au$ requires Au = 33.82 per cent.). This gold salt intumescenced on heating.

Nitroaminomesitylenediazo-β-naphthol,



—The nitrodiamine, diazotised in hydrochloric acid with excess of sodium nitrite, was added to alkaline β-naphthol. The brown precipitate, crystallised repeatedly from benzene, melted at 208–209° (Found: N = 15.99. $C_{19}H_{18}O_3N_4$ requires N = 16.00 per cent.).

6-Nitromesitylenbisazoresorcinol (Formula XIII).—The nitrodiamine hydrochloride, diazotised with a large excess of nitrite, was coupled with aqueous resorcinol after removing excess of

nitrous acid with urea. The bright crimson azo-compound, crystallised repeatedly from glacial acetic acid, was obtained in brown, nodular crystals which did not melt below 290° (Found: N = 15.60. $C_{21}H_{19}O_6N_5$ requires N = 16.02 per cent.).

Triazonitroaminomesitylene (Nitromesidineazoimide) (Formula XII).—Sodium azide was added to a solution of nitroaminomesitylenediazonium chloride, when a yellowish-brown precipitate was formed, soluble in the ordinary organic media. This monotriazo-compound, when crystallised successively from benzene and light petroleum, separated in light yellow rosettes melting at $83-84^{\circ}$ (Found: N = 31.85. $C_9H_{11}O_2N_5$ requires N = 31.68 per cent.). The azide dissolved sparingly in hydrochloric acid and was then diazotisable, yielding with β -naphthol a brown azo-derivative.

Bistriazonitromesitylene (Nitromesitylenebisazoimide, Formula XIV).—To 1 gram of nitrodiaminomesitylene, dissolved in 10 c.c. of 25 per cent. sulphuric acid, were added successively 0.7 gram of sodium azide and 1.5 grams of sodium nitrite. After the addition of nitrite, a further 0.7 gram of sodium azide was introduced and the mixture left in the freezing mixture for half an hour. The brownish-yellow precipitate was crystallised repeatedly from light petroleum, the bistriazo-derivative being then obtained in light yellow needles melting at 50° . It intumescend on heating and evolved nitrogen with concentrated sulphuric acid (Found: N = 40.03. $C_9H_9O_2N_7$ requires N = 39.67 per cent.).

IV.—Diazotisation of Triaminomesitylene.

Triaminomesitylene is not readily prepared by reducing nitrodiaminomesitylene with tin and hydrochloric acid. The reaction proceeded only slowly, and during the long heating required to dissolve the tin the triamine was decomposed hydrolytically with formation of trimethylphloroglucinol.

The reduction of trinitromesitylene to triaminomesitylene with tin and hydrochloric acid in presence of glacial acetic acid was first carried out by Weidel and Wenzel (*Monatsh.*, 1898, **19**, 250). It was found, however, that if heating was prolonged for three to four hours until the tin had dissolved, this led to partial hydrolysis and formation of diaminomesitol. This product was identified by conversion into its bisazide.

Bistriazohydroxyimesitylene (Bistriazomesitol), $(C_6H_5)_3C_6(OH)(N_2)_2$.—Diaminomesitol hydrochloride (1 gram) was dissolved in cold dilute hydrochloric acid and treated successively with 0.75 gram of sodium azide, 1 gram of sodium nitrite, and an additional 0.75 gram of the azide. The product, when crystallised repeatedly from light petroleum, separated in well-defined, colourless needles,

becoming brown on exposure and melting at 67° (Found : C = 49.47; H = 4.97; N = 38.91. $C_9H_{10}ON_6$ requires C = 49.54; H = 4.59; N = 38.53 per cent.).

This bistriazo-derivative resembled diaminomesitol in developing a deep red coloration with ferric chloride, the colour being discharged by acids. It was soluble in aqueous alkali hydroxides, reprecipitated by acid, and decomposed by concentrated sulphuric acid.

We have noticed the difficulty experienced by Forster and Fierz (*loc. cit.*) in the estimation of carbon in these polytriazio-derivatives, the results being generally about 2 per cent. too high. This difficulty was overcome by a wet combustion of the substance (Morgan, T., 1904, 85, 1004), the hydrogen being estimated by the ordinary dry method.

Aminomesitylenebisdiazonium Chloraurate Hydrochloride (Formula XVII).—Triaminomesitylene was most readily obtained by heating on the water-bath for not more than thirty minutes after the vigorous reaction had subsided, 10 grams of trinitromesitylene, 20 c.c. of glacial acetic acid, 48 grams of tin, and 100 c.c. of hydrochloric acid (*d* 1.19). Forty c.c. of glacial acetic acid were then added to the solution, decanted from undissolved tin, and the liquid was cooled in ice, when silvery leaflets of triaminomesitylene stannichloride separated. The mother-liquor yielded on concentration a further crop of the tin salt. This crystalline product was dissolved in 500 c.c. of cold water, and the tin precipitated with hydrogen sulphide. The colourless filtrate from tin sulphide, which rapidly became yellow on exposure to air, was evaporated under reduced pressure in an atmosphere of carbon dioxide, when triaminomesitylene hydrochloride was obtained in colourless needles. The triamine set free by stirring the hydrochloride into concentrated aqueous sodium hydroxide at 0° was a colourless, crystalline mass, which, when crystallised from xylene, separated in yellowish-white needles melting at 118° – 119° . This base was very oxidisable and readily lost its amino-groups by hydrolysis. Consequently in the following experiments the hydrochloride was employed.

One gram of triaminomesitylene trihydrochloride, dissolved in 2.5 c.c. of 10 *N*-hydrochloric acid and 20 c.c. of water, was diazotised with excess of sodium nitrite (one gram = 3.5 mols.). To the solution was added chloroauric acid so long as the light brown, crystalline precipitate was obtained. This salt, which was stable at the ordinary temperature in the dark, exploded on gently warming and darkened on exposure to light (Found : C = 12.31; H = 1.24; N = 8.38, 8.50; Cl = 32.2, 32.6; Au = 44.97. $C_9H_{11}N_5Cl_3Au_2$ requires C = 12.46; H = 1.27; N = 8.07; Cl = 32.75; Au = 45.4 per cent.).

One gram of this trihydrochloride, diazotised in excess of hydrochloric acid, sodium nitrite (3 mols.), and urea, was treated with chloroauric acid, when a brown, crystalline *chloroaurate hydrochloride* was obtained which exploded on warming (Found: Au = 43.37. $C_9H_{12}N_5Cl_6Au_2$ requires Au = 43.63 per cent.).

Bistriazomesidine (Aminomesitylenbisazoimide) (Formula XIX).—Triaminomesitylene hydrochloride (2 grams), dissolved in water acidified with 5 c.c. of hydrochloric acid (*d* 1.16), was treated successively with 1 gram of sodium azide and 1.5 grams of sodium nitrite (3 mols.), the temperature being maintained at -5° . Another gram of sodium azide was then added and the mixture left for one hour. The pale yellow crystals which had separated were recrystallised from light petroleum, when *bistriazomesidine* was obtained in colourless needles melting at 68° (Found: C = 49.6; H = 5.23; N = 44.96. $C_9H_{11}N_7$ requires C = 49.77; H = 5.07; N = 45.18 per cent.). Bistriazomesidine dissolved sparingly in hydrochloric acid and was diazotisable further in the solution; it intumesced on heating rapidly and was decomposed vigorously with evolution of nitrogen by concentrated sulphuric acid.

Tristriazomesitylene (Formula XVIII).—Two grams of triaminomesitylene hydrochloride were dissolved in the least amount of water, and the solution was treated with 10 c.c. of concentrated hydrochloric acid and 1.5 grams of sodium azide. After cooling to -5° , the hydrochloride was diazotised with 3.2 grams of sodium nitrite (6 mols.) and a further 1.5 grams of sodium azide were added. The brownish-yellow crystals which separated were collected after several hours and distilled in steam to free them from tarry impurities. The distillate, which was obtained in a crystalline form mixed with oil, was extracted with ether, and the ethereal extract dried and evaporated. The residue was again distilled in steam, when colourless needles were obtained in the distillate. This product was crystallised from light petroleum, when *tristriazomesitylene* was obtained in soft, colourless needles, becoming brown on exposure to light and melting at 50° (Found: C = 44.90; H = 4.18; N = 51.48. $C_9H_6N_9$ requires C = 44.44; H = 3.70; N = 51.85 per cent.). Tristriazomesitylene was fairly stable and burnt quietly in the Dumas nitrogen estimation. With concentrated sulphuric acid, it reacted vigorously, evolving nitrogen.

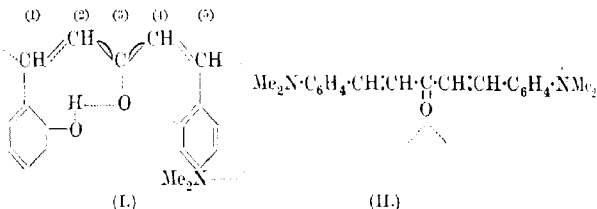
CHEMICAL DEPARTMENT,
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EDGBASTON.

[Received, December 13th, 1922.]

XXXI.—*The Reactivity of Doubly-conjugated Unsaturated Ketones. Part IV. The Effect of Substitution on the Reactivity of 4'-Dimethylamino-2-hydroxydistyryl Ketone.*

By ISIDOR MORRIS HEILBRON and ABRAHAM BRUCE WHITWORTH.

It was shown in Part I of this series of investigations (Heilbron and Buck, T., 1921, **119**, 1500) that 4'-dimethylamino-2-hydroxydistyryl ketone is extraordinarily reactive, but that the effect is largely destroyed on replacing the hydrogen of the free hydroxyl by methyl. It is thus obvious that the *o*-hydroxyl group plays a very prominent part in determining the degree of reactivity of ketones of this type. In order to explain this, the formation of definite ring systems by means of subsidiary valency forces, involving the hydroxyl group and the carbonyl oxygen atom, was postulated (Formula I). The neutralisation of the residual affinity of this oxygen atom would, according to the Pfeiffer hypothesis, enhance the unsaturation of the carbonyl carbon atom (3) and this effect would finally become manifest on the free terminal carbon atom (1) of the conjugated system.



These deductions are a necessary extension of Borsche's theory (*Annalen*, 1910, **375**, 145), who explains the unreactivity of *pp'*-tetramethyldiaminodistyryl ketone and of *pp'*-dimethoxydistyryl ketone by assuming neutralisation of the residual affinities of the terminal carbon atoms of the conjugated system with the dimethyl amino-groups (II).

In order further to test the validity of these views, the effect of substitution in the phenolic residue of the molecule has now been studied. Two points of interest here arise, first, the general effect of the introduction of acidic and basic groupings on the reactivity of the ketones, and, secondly, the special effect due to the position of the substituting group.

With regard to the first point, this has been tested with the com-

pounds shown below, in all of which substitution is in the 5-position. The effects are summarised in the following table :

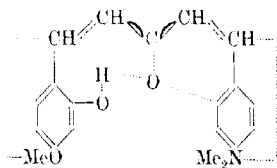
- 4'-dimethylamino-2-hydroxydistyryl ketone—very stable additive compounds.
 4'-dimethylamino-5-methoxy-2-hydroxydistyryl ketone—stable additive compounds.
 5-bromo-4'-dimethylamino-2-hydroxydistyryl ketone—stable solvate additive products only.
 5-nitro-4'-dimethylamino-2 hydroxydistyryl ketone—slightly reactive.

It will be seen that neither by the introduction of basic nor of acidic groups into the molecule is the reactivity increased. Indeed, with the latter, a definite damping effect is noticeable, this being specially marked in the case of the nitro-derivative. It is possible that, in this case, the strongly negative oxygen atoms of the nitro-group exert an attractive influence on the hydrogen atom of the hydroxy-group, thus diminishing the tendency to co-ordinate ring formation with the carbonyl oxygen atom.

Turning now to the consideration of the second point, which has been investigated in detail in the case of the methoxy-derivatives, 4'-dimethylamino-5-methoxy-2-hydroxydistyryl ketone is practically as reactive as the unsubstituted hydroxy-ketone itself. Like that substance, it is separated from the alkaline condensation solution in combination with one molecule of *p*-dimethylaminobenzaldehyde, which addendum is readily replaced by benzene and other solvent addenda. The 3-methoxy-ketone, which one would expect to react quite similarly to the 5-methoxy-derivative, is actually, however, very much less reactive, and fails to form any additive compound with *p*-dimethylaminobenzaldehyde. From solvents, however, crystals of various colours are obtained, obviously due to solvate addition, but, in all cases, the solvent is exceedingly rapidly lost. This ketone exists in two modifications of different melting point. It separates from methyl or ethyl alcohol solution in bright red needles melting at 151°, whereas, crystallised from benzene, chloroform, or ethyl acetate, it melts at 165°. Analyses of both forms show that it is the free ketone which has been obtained. The relative unreactivity of this substance in comparison with the 5-methoxy-derivative can only be explained by assuming some steric effect tending to restrain the hydroxyl-carbonyl ring formation. This suggestion is strengthened, as mentioned later, by the anomalous behaviour observed in the attempted preparation of the simple 3-methoxy-2-hydroxystyryl methyl ketone itself.

With regard to the properties of 4'-dimethylamino-4-methoxy-

2-hydroxydistyryl ketone, this substance is totally unreactive. It crystallises from various solvents in exactly the same crystalline form and colour, and shows no indication whatsoever of any tendency to form solvent or other addenda. We consider that the inactivity of this compound strongly supports the views expressed, for obviously, in this derivative, the conditions postulated by Borsche again obtain, complete neutralisation of all free valency forces taking place, as illustrated in the following formula:



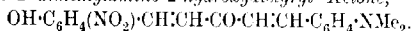
The ketones described in this paper were prepared in the usual manner by condensation of the substituted salicylaldehyde with acetone, and the further condensation of the resulting styryl methyl ketones with *p*-dimethylaminobenzaldehyde in presence of alkali. As the exact methods employed for each individual ketone are described in the experimental part, it is only necessary here to draw attention to the abnormality observed in the condensation of 3-methoxysalicylaldehyde with acetone. The product obtained in this case proved, on analysis, to contain an additional molecule of water, which was not removed either on boiling with acetic anhydride or in benzene solution with phosphoric oxide. It would thus appear that condensation had taken place, yielding the aldol rather than the unsubstituted ketone. Attempts to prove this point by the preparation of the *dibenzoyl* derivative failed to produce the desired product, the normal *mono-benzoyl* derivative minus the extra molecule of water being obtained. It is noteworthy that this molecule of water is also eliminated on condensation with *p*-dimethylaminobenzaldehyde, the normal distyryl ketone being obtained. It is highly probable, however, that the product is actually β -hydroxy- β -3-methoxy-2-hydroxyphenylethyl methyl ketone, for, whereas the styryl methyl ketones usually become darker in colour on standing in air, owing to surface oxidation, this substance shows no such tendency. It would thus seem that the presence of the methoxy-group adjacent to the hydroxyl directly influences the character of the molecule both in the styryl methyl ketone as also in the distyryl derivative.

EXPERIMENTAL.

5-Nitro-2-hydroxystyryl Methyl Ketone.—Twenty grams of 5-nitrosalicylaldehyde were dissolved by warming in 200 c.c. of 2*N*-sodium

hydroxide, and when quite cold, 40 grams (6 mols.) of acetone were added. The solution, which rapidly became deep red, was kept for three days and the free ketone precipitated by means of dilute acetic acid. After two crystallisations from acetone, it was obtained in yellow crystals melting at 227° , moderately soluble in acetone or ethyl acetate, very sparingly soluble in alcohol, chloroform, or ether (Found: $N = 6.8$. $C_{10}H_9O_4N$ requires $N = 6.8$ per cent.).

5-Nitro-4'-dimethylamino-2-hydroxydistyryl Ketone,

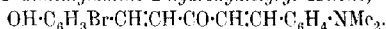


—Five grams of the above ketone were dissolved in alcohol together with an equal weight of *p*-dimethylaminobenzaldehyde and treated with 40 per cent. sodium hydroxide solution (3 mols. of NaOH). The solution, which soon acquired a very deep red colour, was kept at room temperature for three days and the precipitated ketone filtered off and washed with alcohol. It was purified by crystallisation, first from alcohol containing a few drops of glacial acetic acid, and finally from absolute alcohol itself. It crystallised with 1 mol. of ethyl alcohol in dark red needles melting at 238° (Found: $N = 7.1$. $C_{19}H_{18}O_4N_2 \cdot C_2H_5 \cdot OH$ requires $N = 7.3$ per cent.). The alcohol addendum is gradually lost at the ordinary temperature, rapidly in the steam-oven, yielding the solvent-free substance. The ketone has also been prepared by condensation of 5-nitrosalicylaldehyde with *p*-dimethylaminostyryl methyl ketone. Ten grams of the sodium salt of 5-nitrosalicylaldehyde were dissolved in 400 c.c. of *N*/₄-sodium hydroxide and mixed with a solution of *p*-dimethylaminostyryl methyl ketone (1 mol.) in pyridine, sufficient alcohol being then added to prevent separation of the two liquids. After four days, the ketone was filtered off and crystallised from acetone (Yield: 8 grams) (Found: $N = 8.0$. $C_{19}H_{18}O_4N_2$ requires $N = 8.3$ per cent.).

5-Bromo-2-hydroxystyryl Methyl Ketone.—This compound has previously been prepared by Kostanecki (*Ber.*, 1896, **29**, 1892), but no details of his method are given. After trying various conditions, the following procedure was found to give the most satisfactory yield. Twenty grams of 5-bromosalicylaldehyde were dissolved in 80 c.c. of 10 per cent. sodium hydroxide solution, 25 grams of acetone (4 mols.) added, and the solution was diluted to a total volume of 500 c.c.; after three or four days, it was further diluted with water to twice its volume and slowly poured, with continual stirring, into an ice-cold solution of *N*-hydrochloric acid. The flocculent precipitate obtained in this way was filtered off and the crude product (25 grams) purified by recrystallisation from benzene. If the condensation liquor is not kept at least at the above dilution, or if warmed, reaction takes place in such a manner that

the symmetrical distyryl ketone is mainly produced and precipitated from the alkaline solution in the form of its sodium salt. 5-Bromo-2-hydroxystyryl methyl ketone forms pale yellow crystals melting at 154—155°.

5-Bromo-4'-dimethylamino-2-hydroxydistyryl Ketone,



—Twenty grams of 5-bromo-2-hydroxystyryl methyl ketone and 18 grams (1.5 mols.) of *p*-dimethylaminobenzaldehyde were dissolved in alcohol and treated with 70 c.c. of 10 per cent. sodium hydroxide (2 mols.). The solution, which at once became deep red, was kept for two days, after which the precipitate which had separated out was filtered off and washed with alcohol. Nine grams of a brick-red solid were thus obtained, which, after recrystallisation from alcohol, formed a characteristic felt-like mass of crystal aggregates containing sodium, quite analogous to the sodium complex obtained by Heilbron and Buck (*loc. cit.*) in the case of 4'-dimethylamino-2-hydroxydistyryl ketone. The free ketone was readily formed from this complex by recrystallisation from alcohol containing a small quantity of glacial acetic acid. The main yield of the ketone was, however, obtained by pouring the mother-liquors slowly into ice-cold water with rapid stirring, when it separated as a dark red, crystalline precipitate (Yield: 20 grams). Crystallisation from solvents yields solvate additive compounds, from which the free ketone is again obtained in orange-coloured crystals melting at 194° by heating in the steam-oven for a few hours (Found: N = 3.9. $\text{C}_{19}\text{H}_{18}\text{O}_2\text{NBr}$ requires N = 3.8 per cent.).

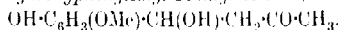
Additive Products.—With ethyl alcohol: $\text{C}_{19}\text{H}_{18}\text{O}_2\text{NBr}\cdot\text{C}_2\text{H}_6\text{O}$. This forms glistening, crimson needles with violet lustre (Found: C = 60.2; H = 5.8; N = 3.6. Calc., C = 60.5; H = 5.8; N = 3.4 per cent.).

With benzene: $\text{C}_{19}\text{H}_{18}\text{O}_2\text{NBr}\cdot\text{C}_6\text{H}_6$. Red, needle-shaped crystals (Found: C = 67.1; H = 5.4. Calc., C = 66.9; H = 5.4 per cent.).

With ethyl acetate: $\text{C}_{19}\text{H}_{18}\text{O}_2\text{NBr}\cdot\text{C}_4\text{H}_8\text{O}_2$. Orange-coloured needles (Found: C = 60.2; H = 5.7. Calc., C = 60.1; H = 5.6 per cent.).

With chloroform: with 1 mol., glistening green plates (Found: C = 48.9; H = 4.1. Calc., C = 48.9; H = 3.9 per cent.). With $\frac{1}{2}$ mol., yellow, felted, crystal clusters. These are obtained by slow crystallisation from chloroform (Found: C = 54.4; H = 4.6. Calc., C = 54.4; H = 4.3 per cent.).

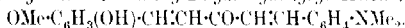
3-Methoxy-2-hydroxydistyryl Methyl Ketone + H₂O or β-Hydroxy-β-3-methoxy-2-hydroxyphenylethyl Methyl Ketone,



—Twenty grams of *m*-methoxysalicylaldehyde were dissolved in

32 grams (4 mols.) of acetone, and 240 c.c. of 2.5 per cent. sodium hydroxide solution added. A further 60 c.c. of 10 per cent. sodium hydroxide solution was then gradually added in small quantities at a time over a period of one hour, when the solution became an intense red. Water (600 c.c.) was now added and the whole left for two days at room temperature. The solution was then diluted to two litres and slowly acidified with dilute hydrochloric acid. The flocculent, yellow precipitate, which gradually became crystalline on standing, was filtered, dried, and the ketone purified by recrystallisation from benzene. It formed pale yellow plates, melting at 83°, and proved on analysis to contain a molecule of water exceedingly firmly held and not split off either by boiling in benzene solution with phosphoric oxide or acetic anhydride (Found : C = 62.6; H = 6.9. $C_{11}H_{12}O_3 + H_2O$ requires C = 62.8; H = 6.7 per cent.). In order to ascertain whether the molecule of water was present as an integral part of the molecule, the ketone was benzoylated in the following manner : To 2 grams of the compound, dissolved in 125 c.c. of ether, 10 grams of benzoyl chloride were added alternately with pyridine in small quantities at a time, care being taken to maintain throughout a slight excess of the base. After several days the solution was filtered from precipitated pyridine hydrochloride and washed first with sodium carbonate solution and then with water until free from pyridine. After drying over calcium chloride, the ether was distilled off and the solid residue purified by crystallisation from an ether-ligroin mixture. Analysis of this compound, which is obtained in colourless, star-like clusters melting at 120°, shows it to correspond to a *monobenzoyl* derivative of the unsaturated ketone (Found : C = 72.9; H = 5.4. $C_{18}H_{16}O_4$ requires C = 73.0; H = 5.4 per cent.).

4'-Dimethylamino-3-methoxy-2-hydroxydistyryl Ketone.



—Owing to the sparing solubility of the sodium salt of the above ketone, it was found necessary to carry out the condensation in the warm. Twenty grams of the ketone were dissolved in 250 c.c. of alcohol, 80 c.c. of 10 per cent. sodium hydroxide were added, and the solution was warmed to 50°. A solution containing 23 grams (1.5 mols.) of *p*-dimethylaminobenzaldehyde in 100 c.c. of alcohol was next added, and the whole maintained at 50° for two days. On allowing to cool, a dark crimson, felted mass separated out. This was filtered off, repeatedly washed with water, and recrystallised from alcohol containing a few drops of glacial acetic acid. After a further recrystallisation from absolute alcohol itself, the ketone was obtained in bright red needles melting sharply at 151°. A second modification of this substance has also been obtained on crystallisation of

the 151°-compound from benzene, when violet needles are obtained, melting at 165°. This probably corresponds with an additive compound of the ketone with benzene, but the addendum is exceedingly labile and the free ketone readily obtained in dark crimson needles on exposing the solvate compound to air. Crystallisation of the free ketone of either melting point from chloroform yields a mixture of green and orange crystals, which rapidly lose chloroform, giving the red, solvent-free product of m. p. 165°. This can again be converted into the 151°-modification by recrystallisation from either absolute alcohol or methyl alcohol (Found: for 165°-compound, C = 74.3; H = 6.4; N = 4.3. For 151°-compound, C = 73.9; H = 6.3; N = 4.2. $C_{20}H_{21}O_3N$ requires C = 74.3; H = 6.5; N = 4.33 per cent.).

4-Methoxy-2-hydroxystyryl Methyl Ketone,
 $OMe \cdot C_6H_5(OH) \cdot CH:CH \cdot CO \cdot CH_3$.

—4-Methoxysalicylaldehyde was prepared by Ott and Nauen's method (*Ber.*, 1922, 55, [B], 920) and the condensation carried out as described in the preparation of the 3-methoxy-derivative. The crude ketone, which was purified by crystallisation from benzene, using animal charcoal as decolorising agent, formed pale yellow crystals melting at 131°. It is readily soluble in alcohol, acetone, or chloroform, sparingly soluble in benzene, and practically insoluble in light petroleum. On standing in air, it tends to oxidise, assuming a green colour (Found: C = 68.6; H = 6.3. $C_{11}H_{12}O_3$ requires C = 68.8; H = 6.3 per cent.).

4'-Dimethylamino-4-methoxy-2-hydroxydistyryl Ketone.—The condensation of 4-methoxy-2-hydroxystyryl methyl ketone with *p*-dimethylaminobenzaldehyde is extremely difficult to bring about and was only done by employing 50 per cent. sodium hydroxide as the condensing agent. Four grams of the ketone together with 5 grams of *p*-dimethylaminobenzaldehyde were dissolved in 25 c.c. of alcohol and to the warm solution 3 c.c. of 50 per cent. sodium hydroxide at 76° were now added. After shaking for a few minutes, and keeping for a few hours, the semi-solid mass thus formed was agitated, first with a large volume of water, and finally with dilute acetic acid, filtered, and dried. After two crystallisations from alcohol, it was obtained in purple crystals melting with decomposition at 183°. In no case could any indication of the formation of additive products be noted, crystallisation from chloroform, benzene, or ethyl acetate immediately yielding the free ketone. Various attempts were also made to form a *p*-dimethylaminobenzaldehyde additive product, but even in the presence of alkali the ketone remained totally unreactive (Found: C = 74.3; H = 6.4; N = 4.3. $C_{20}H_{21}O_3N$ requires C = 74.3; H = 6.5; N = 4.33 per cent.).

5-Methoxy-2-hydroxystyryl Methyl Ketone.—This ketone was prepared from 5-methoxysalicylaldehyde by the general method. It crystallises from benzene in bright yellow needles (m. p. 122°), readily soluble in alcohol, ether, or acetone, and somewhat sparingly soluble in benzene. Like these styryl ketones in general, it gives a deep red coloration with concentrated sulphuric acid (Found: C = 68.7; H = 6.3. $C_{11}H_{12}O_3$ requires C = 68.8; H = 6.3 per cent.).

4'-Dimethylamino-5-methoxy-2-hydroxydistyryl Ketone.—Fifteen grams of 5-methoxy-2-hydroxystyryl methyl ketone and 20 grams (1.5 mols.) of *p*-dimethylaminobenzaldehyde were dissolved in 250 c.c. of alcohol, and 60 c.c. of 10 per cent. sodium hydroxide solution (2 mols.) added. After keeping for three days at the ordinary temperature, the reaction product was poured into two litres of ice-cold water, and the crystalline precipitate, which gradually separated out, was filtered off and thoroughly washed with water. On recrystallisation from absolute alcohol, the ketone + 1 mol. *p*-dimethylaminobenzaldehyde was obtained in bright red plates melting at 110° (Yield: 10 grams.) The same additive product can also be obtained from the free ketone by dissolving the two components in hot alcohol and allowing the solution to crystallise (Found: C = 73.8; H = 6.9; N = 6.0. $C_{20}H_{21}O_3N.C_9H_{11}ON$ requires C = 73.7; H = 6.8; N = 5.9 per cent.). On boiling this double compound with benzene for about two hours, there crystallise out glistening, greenish-purple leaflets which melt sharply at 120° (rapid heating), and prove to be the *benzene* additive product, the *p*-dimethylaminobenzaldehyde having been displaced by a half-molecule of benzene (Found: N = 3.9. $C_{20}H_{21}O_3N.\frac{1}{2}C_6H_6$ requires N = 3.9 per cent.). On heating this additive compound in the steam-oven for several hours, the free ketone is obtained in dark crimson needles, melting at 151° (Found: C = 74.0; H = 6.7. $C_{20}H_{21}O_3N$ requires C = 74.3; H = 6.5 per cent.). The *ethyl acetate* additive product, obtained by dissolving the free ketone in ethyl acetate and precipitating with light petroleum, forms characteristic, black, glistening nodules (Found: N = 3.4. $C_{20}H_{21}O_3N.C_4H_8O_2$ requires N = 3.4 per cent.).

In conclusion, we desire to express our thanks to the Governors of the Royal Technical College, Glasgow, for an Exhibition to one of us (A.B.W.) which has enabled this work to be carried out.

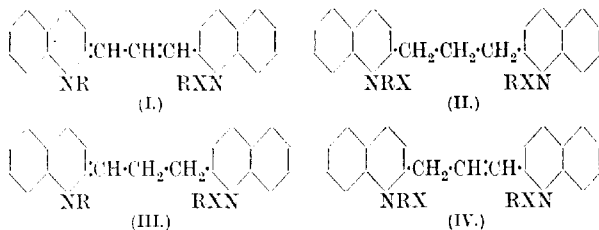
DEPARTMENT OF ORGANIC CHEMISTRY,

THE UNIVERSITY, LIVERPOOL. [Received, December 21st, 1922.]

XXXII.—*Some Derivatives of Methylenediquinaldine and their Relationship to the Carbocyanines.*

By FRANCES MARY HAMER.

It has been shown by Mills and Hamer that the photographic sensitiser known as pinacyanol may be represented by formula 1 (T., 1920, **117**, 1550). As regards the mechanism of the carbo-cyanine condensation, we suggested that when alkali

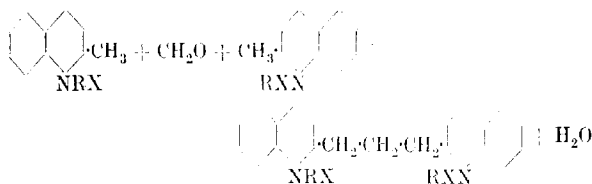


acts upon a solution of quinaldine ethiodide, in presence of a quinolinium salt, the first product may be methylenediquinaldine diethiodide (II), which subsequently loses hydriodic acid, giving III, and that from this the carbo-cyanine is produced, by an oxidation involving the removal of two hydrogen atoms. It is, on the other hand, conceivable that oxidation of the hypothetical methylenediquinaldine diethiodide may precede the elimination of halogen acid, in which case the second intermediate product would be IV* instead of III. These considerations show that, apart from the inherent interest of compounds of the methylenediquinaldine type, the realisation of their preparation was especially desirable in order that their relationship to carbo-cyanine might be put to the test; could the dialkylhalide (II) be made the starting point for the synthesis of such a dye, this would afford valuable confirmation of the pinacyanol formula (I), which differs from the other formulæ which have been suggested (Fischer, *J. pr. Chem.*, 1918, [ii], **98**, 204; Wise, Adams, Stewart, and Lund, *J. Ind. Eng. Chem.*, 1919, **11**, 460) in that the two quinoline nuclei are linked in the α -positions by a chain of three carbon atoms. It is with this object that the present investigation was undertaken.

Although methylenediquinaldine is theoretically obtainable by condensation of two molecules of quinaldine with one of formaldehyde, yet it has never been described, although the interaction

* Guia has recently described a substance which he imagines to be the base of which IV is the diethiodide (*Gazzetta*, 1922, **52**, i, 349).

of these reagents was studied, first by Methner (*Ber.*, 1894, **27**, 2689), and subsequently more thoroughly by Koenigs (*Ber.*, 1899, **32**, 223). A general method of preparation of the dialkylhalides of methylenediquinaldine resulted, however, from the discovery of a hitherto unknown reaction between two molecules of quinaldine alkylhalide and one of formaldehyde, in presence of piperidine; this may be represented by the following equation:



Thus from quinaldine methiodide and formaldehyde, methylenediquinaldine dimethiodide was obtained, and it was so slightly soluble in absolute alcohol as to separate even from the boiling reaction liquid. From it, by treatment with the appropriate silver salt, the dimethonitrate and the dimethochloride were prepared, and this latter was converted into the corresponding dimethobromide. In preparing methylenediquinaldine diethiodide, a modification of the method was necessary because quinaldine ethiodide is insufficiently soluble in alcohol to give a solution of the requisite concentration: quinaldine ethochloride is, however, suitable and its condensation product with formaldehyde was converted by means of potassium iodide into methylenediquinaldine diethiodide. By reaction of 6-methylquinaldine ethiodide with formaldehyde there was prepared 6:6'-dimethylmethylenediquinaldine diethiodide.

A consideration of numerous analogous reactions (compare Decker, *Ber.*, 1905, **38**, 2493; Mills, T., 1922, **121**, 455) led to the expectation that the effect of alkali on methylenediquinaldine dialkylhalide would be the elimination of halogen acid, giving a compound of type III. It was, however, found that the dialkylhalides are comparatively stable towards alkalis in the cold, whilst, on warming, a mixture containing a small percentage of carbocyanine is produced. A quantitative experiment with hot alcoholic soda showed the yield of pure dye to be less than 4 per cent. of the theoretical. It was not increased by the action, together with the alkali, of various oxidising agents, such as air, *p*-benzoquinone, or hydrogen peroxide.

Now the ordinary preparation of carbocyanine is brought about by the action of alkali on an alcoholic solution of quinaldine ethiodide,

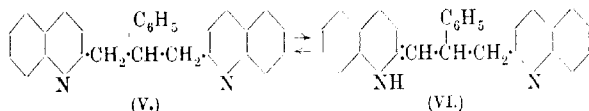
R* 2

quinoline ethiodide, and formaldehyde, and it has been shown that the quinoline ethiodide plays no direct part in the condensation, but that, in its absence, a poorer yield is obtained (Mills and Hamer, *loc. cit.*). It was possible, therefore, that the addition of a quinolinium quaternary salt might also promote the conversion of methylenediquinaldine dimethiodide into carbocyanine. This proved to be the case, for when soda was allowed to act upon an alcoholic solution of the dimethiodide, in presence of quinoline methiodide, the yield of dye was tenfold that obtained in its absence. Thus the transformation of the dimethiodide of methylenediquinaldine into carbocyanine provides definite evidence of relationship between the two and confirms the pinacyanol formula (I). The possibility that the carbocyanine was derived not solely from methylenediquinaldine dimethiodide, but also from the quinolinium salt, was put to the test by using the ethiodide instead of the methiodide of quinoline, for the introduction of an extra methylene group into the molecule of the product would be capable of analytical detection. The dye was, however, identified as 1:1'-dimethylcarbocyanine iodide by its appearance, melting point and mixed melting point, absorption and sensitising bands, as well as by analysis. The same compound was obtained when 6-methylquinoline ethiodide was used instead of the unsubstituted substance. It was thus proved that the quinoline quaternary compound plays no direct part in the production of carbocyanine. This conclusion was confirmed by the action of alkali on methylenediquinaldine diethiodide in presence of quinoline methiodide, when the product was 1:1'-diethylcarbocyanine iodide, as also by its action on 6:6'-dimethylmethylenediquinaldine diethiodide in presence of quinoline methiodide, when 6:6'-dimethyl-1:1'-diethylcarbocyanine iodide was obtained. Another possibility to be considered was that the methylenediquinaldine dialkylhalide might, by the influence of soda, be split into quinaldine alkylhalide and formaldehyde, which subsequently reacted in the normal manner. But this is disproved because, in an ordinary carbocyanine condensation, the yield of pure product is only about one-fifth of that theoretically obtainable, whereas the yields under optimum conditions in the four preparations above described varied from 38—47 per cent. of the theoretical.

The part enacted by the quinolinium salt in this condensation, as in that ordinarily used for the preparation of carbocyanine, is still obscure. Although theoretically the removal of two hydrogen atoms and of a molecule of halogen acid from that of methylenediquinaldine dimethiodide would transform it into carbocyanine, yet it is significant that, apart from quinoline alkylhalide, no

oxidising agent was found which, in conjunction with alkali, brought about this conversion. Whilst 6-methylquinoline ethiodide could satisfactorily play the part of the unsubstituted salt, this was not the case when the methyl group occupied the 2-position, for with quinaldine methiodide there was a considerable diminution in the yield; the methiodide of pyridine was quite useless. It is clear, then, that the action of the quinoline quaternary salt is a highly specific one and the yield is closely dependent on the amount added.

Benzylidenediquinaldine (V) was prepared in order to ascertain whether, from the methiodide of the base, it was possible to synthesise 10-phenyl-1:1'-dimethylcarbocyanine iodide. Although

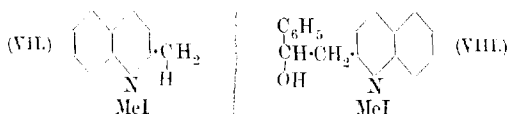


this base was described by Koenigs as a colourless, viscous fluid, which could not be crystallised (*Ber.*, 1899, **32**, 3599), it was now obtained as white prisms, by slow evaporation of the solvent from a dry, concentrated, ethereal solution. The solid, which melted at 90–94° to a cloudy liquid, was converted by heat into a white substance of melting point 106.5–107.5°, and this change was unaccompanied by change in weight. The reverse transformation was effected by dissolving the compound of higher melting point in absolute ether and allowing the solvent to evaporate. Complete analyses of each substance gave the values required for anhydrous benzylidenediquinaldine, whilst their chemical properties were identical. Now Scheibe suggested that the isomerism of the related substance, diquinolymethane, is due to the transformation of one benzenoid pyridine ring into an orthoquinonoid form (*Ber.*, 1921, **54**, [B], 786): if a similar explanation be applied to the isomerism of benzylidenediquinaldine, the two desmotropes would be V and VI. Benzylidenediquinaldine differs from diquinolymethane in that the monacid salts appear to be colourless like the diacid derivatives; only compounds of the latter type were actually isolated and of these the dinitrate had not previously been described. The most striking property of the white dihydrochloride was its invariable assumption of a pink tint in the dark, but, on exposure to sunlight, it was instantaneously restored to its colourless condition.

When either form of benzylidenediquinaldine was heated with methyl iodide in a sealed tube at 55–60°, the dimethiodide was formed. Slight lowering of the reaction temperature had so great an influence that at 40–50° practically pure monomethiodide

resulted, even when a large excess of methyl iodide was present. The formation of both methiodides of benzyldenediquinaldine contrasts with the behaviour of dibenzothiazolymethane, which reacted as a monacid base towards ethyl iodide (Mills, *loc. cit.*).

It was found that the mono- and di-methiodides of benzyldenediquinaldine are very sensitive to the action of alkali, although there was no development of a carbocyanine colour. Instead of eliminating hydriodic acid from benzyldenediquinaldine dimethiodide, alkali brought about complete disruption of the molecule, as was shown by the production of tar smelling of benzaldehyde. The salt was in fact so unstable that even one recrystallisation from water lowered the percentage of iodine by about 2; by repeated recrystallisation, pure benzyldenediquinaldine methiodide was isolated. Probably the mechanism of the reaction is a hydrolysis, involving formation of quinaldine methiodide (VII), together with compound VIII, which subsequently loses the elements of water.



The observation that calcium carbonate liberated benzaldehyde and a tar from a benzyldenediquinaldine alkylhalide harmonises with the conclusion that the action of alkali is to accelerate the hydrolysis of benzyldenediquinaldine dimethiodide and, moreover, to decompose the resulting benzyldenediquinaldine methiodide.

An experiment strictly comparable with that which sufficed for the conversion of benzyldenediquinaldine dimethiodide into the methiodide of benzyldenediquinaldine was made on methylenediquinaldine dimethiodide, but the latter showed practically no evidence of decomposition. It was therefore concluded that the stability of the molecule is decreased by the presence of the phenyl group.

The mode of decomposition of benzyldenediquinaldine dimethiodide suggested the possibility that methylenediquinaldine dimethiodide may behave similarly, so that, when it is treated with alkali in presence of quinoline ethiodide, the production of methylenediquinaldine methiodide and of quinaldine methiodide may precede carbocyanine formation. There was, however, no indication that this was the case, but, on the contrary, the smooth conversion of methylenediquinaldine dimethiodide into carbocyanine rendered the formation of these intermediate compounds highly improbable. When alkali acted upon a solution of methylenediquinaldine dimethiodide and quinoline ethiodide in presence of quinaldine

ethiodide (or of the methiodide or ethiodide of 6-methylquinaldine), which might combine with the hypothetical methylenequinaldine methiodide to form a second carbocyanine, it is true that pure 1:1'-dimethylcarbocyanine iodide could not be isolated from the product, which on recrystallisation formed a curious gelatinous mass of very fine needles. There was, however, no evidence that the phenomenon was due to contamination by another carbocyanine rather than by impurity of a different nature; with the dye formed from methylenediquinaldine dimethiodide in presence of the methiodide of quinaldine, where there could be no question of a second carbocyanine, the substance crystallised in the ordinary way, but there was produced an abnormally large amount of foreign matter, while the yield of recrystallised carbocyanine was low.

EXPERIMENTAL.

The Methylenediquinaldine Dialkylhalides.

Methylenediquinaldine Dimethiodide.—One mol. of 40 per cent. formaldehyde solution (3·6 grams) and $2\frac{1}{2}$ mols. of quinaldine methiodide (37·2 grams) were dissolved in absolute alcohol (120 c.c.), and the mechanically stirred mixture was boiled gently. An alcoholic solution (3 c.c.) of piperidine (6 drops) caused instant darkening in colour, and the separation of solid began after five minutes; heating was continued for half an hour. The solid was filtered hot, with the object of removing unchanged quinaldine methiodide, and it was further extracted with boiling absolute alcohol (120 c.c.). The yield of crude product was nearly 80 per cent. of the theoretical. Its solution in $1\frac{1}{2}$ per cent. hot aqueous hydrochloric acid was boiled and the hot filtrate was treated with an aqueous solution of potassium iodide. The orange needles of methylenediquinaldine dimethiodide were filtered, washed with acetone, and dried in a vacuum, and the yield was 64 per cent. of the theoretical. When the substance which had been dried at the ordinary temperature was further heated in a vacuum at $60\text{--}70^\circ$, it lost water of crystallisation and gave an anhydrous form of deeper tint (Found: C = 47·67; H = 4·22; N = 4·77; I = 43·40. $\text{C}_{25}\text{H}_{24}\text{N}_2\text{I}_2$ requires C = 47·42; H = 4·16; N = 4·82; I = 43·61 per cent. Loss on drying = 2·9. $\text{C}_{25}\text{H}_{24}\text{N}_2\text{I}_2 \cdot \text{H}_2\text{O}$ requires H_2O = 3·0 per cent.). Melting occurred sharply, but the exact point varied, according to the rate of heating, between 204° and 210° , and it was followed by decomposition. The dimethiodide was very slightly soluble in absolute alcohol, but more so in rectified spirit. It was insoluble in ether, and very slightly soluble in hot chloroform or hot acetone. It dissolved readily in hot water: a solution of

1 gram in 20 c.c. was boiled for three hours, and the product was recrystallised three times more and washed with acetone (Found: I = 43.49 per cent.). The m. p. of the salt, of the original dimethiodide, and of the mixture was 210°. It was therefore concluded that methylenediquinaldine dimethiodide is stable to boiling water.

Methylenediquinaldine Dimethochloride.—An alcoholic solution of methylenediquinaldine dimethiodide (3 grams), acidified with hydrochloric acid, was boiled with excess of silver chloride and, on evaporating the filtrate, the theoretical yield of methylenediquinaldine dimethochloride was obtained. By dissolving it in hot absolute alcohol containing a couple of drops of hydrochloric acid and adding acetone until the commencement of separation, the methochloride took the form of chalky, white needles, which became pale blue on desiccation. A three times crystallised specimen was dried in a vacuum at 60–70°, but from the analysis it would seem that, even under this treatment, pure anhydrous salt did not result (Found: C = 65.26; H = 6.11; N = 6.53; Cl = 16.85. $C_{23}H_{24}N_2Cl_2 \cdot H_2O$ requires C = 66.18; H = 6.28; N = 6.72; Cl = 17.00 per cent.). When heated, darkening began at about 145° and the compound melted to a blue liquid at 184–186°, with decomposition both before and after liquefaction. The methochloride was very hygroscopic. It was extremely soluble in water and also very soluble in alcohol, but slightly so in acetone and almost insoluble in pyridine.

Methylenediquinaldine Dimethobromide.—The twice recrystallised dimethochloride (1.5 grams) was dissolved in hot water with a little hydrochloric acid and was treated with a hot aqueous solution of twice the calculated quantity of potassium bromide. On recrystallising the product from absolute alcohol with a drop of hydrobromic acid, the yield of pure methylenediquinaldine dimethobromide was 71 per cent. of the theoretical. The colourless needles on desiccation acquired a pale blue tint. The salt which had been dried in the steam-oven contained a molecule of water of crystallisation (Found: Br = 31.85. $C_{23}H_{24}N_2Br_2 \cdot H_2O$ requires Br = 31.57 per cent.). This was lost on further heating in a vacuum at 80–90° (Found: loss = 3.5. $C_{23}H_{24}N_2Br_2 \cdot H_2O$ requires H_2O = 3.6 per cent.), giving the anhydrous salt (Found: Br = 32.95. $C_{23}H_{24}N_2Br_2$ requires Br = 32.74 per cent.). On heating, blackening began at 175° and the dimethobromide melted at 180–185°. It was less soluble in alcohol or water than was the corresponding methochloride, but much more so than the iodide.

Methylenediquinaldine Dimethonitrate.—Methylenediquinaldine dimethiodide (1.8 grams) was dissolved in hot water (50 c.c.),

acidified with nitric acid (5 drops), and an aqueous solution of the calculated quantity of silver nitrate was added. The product (1.1 grams) obtained by evaporation of the filtrate was recrystallised from absolute alcohol, in which it was moderately soluble. Its pink colour was not lessened by a second recrystallisation, with charcoal treatment. For analysis it was dried in the steam-oven (Found: $\text{NO}_3 = 27.39$. $\text{C}_{25}\text{H}_{24}\text{N}_2(\text{NO}_3)_2$ requires $\text{NO}_3 = 27.42$ per cent.). When heated, decomposition began at 120° and the substance had become quite black before the melting point, $178\text{--}180^\circ$, was attained. It was stable towards the oxidising action of dilute nitric acid.

Methylenediquinaldine Diethiodide.—In the preparation of methylenediquinaldine diethiodide, quinaldine ethiodide was not employed because of its insufficient solubility. Quinaldine ethochloride (9.3 grams; $2\frac{1}{2}$ mols.) and 40 per cent. formalin (1.3 grams; 1 mol.) were dissolved in absolute alcohol (35 c.c.) and treated with piperidine (2 drops). After half an hour's heating, no solid had separated, but an aqueous solution of potassium iodide (10 grams) precipitated the diethiodide of methylenediquinaldine (9.8 grams). The method of purification was the same as for the dimethiodide and, after heating the yellow crystals in the steam-oven, the yield was 46 per cent. of the theoretical (Found: $\text{C} = 49.03$; $\text{H} = 4.72$; $\text{N} = 4.76$; $\text{I} = 41.54$. $\text{C}_{25}\text{H}_{28}\text{N}_2\text{I}_2$ requires $\text{C} = 49.18$; $\text{H} = 4.63$; $\text{N} = 4.59$; $\text{I} = 41.61$ per cent.). Decomposition began at about 200° and the melting point was $204\text{--}207^\circ$, according to the rate of rise of temperature. The diethiodide is much more soluble in alcohol than is the corresponding dimethiodide.

6:6'-Dimethylmethylenediquinaldine Diethiodide.—This was prepared from 6-methylquinaldine ethiodide (15.5 grams) and separated on cooling the alcoholic solution. It was recrystallised once, with charcoal treatment, from water containing a drop or two of hydrochloric acid, and the yield was 33 per cent. of the theoretical. The pale yellow needles became orange on heating in a vacuum at $80\text{--}90^\circ$, but were then extremely hygroscopic (Found: $\text{I} = 39.32$. $\text{C}_{27}\text{H}_{32}\text{N}_2\text{I}_2$ requires $\text{I} = 39.77$ per cent.). The substance dried over sulphuric acid at the ordinary temperature contained water of crystallisation (Found: $\text{C} = 49.77$; $\text{H} = 5.36$; $\text{N} = 4.25$; $\text{I} = 38.73$. $\text{C}_{27}\text{H}_{32}\text{N}_2\text{I}_2 \cdot \text{H}_2\text{O}$ requires $\text{C} = 49.38$; $\text{H} = 5.22$; $\text{N} = 4.27$; $\text{I} = 38.68$ per cent.).

The Action of Alkalis on Methylenediquinaldine Dialkylhalides.

It was found that the action of alkalis in the cold did not effect the removal of halogen acid to any considerable extent, whilst, on heating, a small amount of carbocyanine was produced.

An alcoholic solution (50 c.c.) of 3 mols. of sodium (0.34 gram) was added to a boiling solution of 1 mol. of methylenediquinaldine dimethiodide (3 grams) in rectified spirit (350 c.c.) and $\frac{1}{2}$ mol. of hydrochloric acid. During twenty minutes' heating, a blue colour gradually developed. Recrystallisation of the product (0.16 gram) from methyl alcohol gave pure carbocyanine (0.08 gram), but the yield was less than 4 per cent. of the theoretical. At 0°, alcoholic soda only caused the development of a carbocyanine colour after some hours.

Preparation of 1:1'-Dimethylcarbocyanine Iodide from Methylene-diquinaldine Dimethiodide.

One mol. of methylenediquinaldine dimethiodide (3 grams) and 2 mols. of quinoline ethiodide (2.85 grams) were dissolved in hot rectified spirit (350 c.c.) with $\frac{1}{2}$ mol. of hydrochloric acid (25 c.c. of *N*/10), and the solution was stirred mechanically and gently boiled. A solution of $3\frac{1}{2}$ mols. of sodium (0.40 gram) in absolute alcohol (50 c.c.) was run in, and the mixture heated for fifteen minutes. On addition of the soda, a green colour momentarily appeared, to be succeeded by blue, and carbocyanine crystallised from the still boiling liquid. A little glacial acetic acid was added (2 c.c.) and on the next day the red fluid was filtered. The crude product was washed with hot alcohol, when the yield was 56 per cent. of the calculated amount. After recrystallisation from methyl alcohol, the total yield of anhydrous product (0.95 gram) was 42 per cent. For analysis, it was dried in a vacuum at 120–130° until of constant weight (Found: C = 61.14; H = 4.75; N = 6.19; I = 28.10. $C_{23}H_{21}N_2I$ requires C = 61.05; H = 4.68; N = 6.20; I = 28.06 per cent.). The substance melted with decomposition at 278°; melting at exactly the same temperature occurred in the case of a specimen of 1:1'-dimethylcarbocyanine iodide prepared in the usual manner, and of a mixture of the two, all three melting points being observed simultaneously. The absorption and sensitising bands were photographed, by the method described elsewhere (Hamer, *Phot. J.*, 1922, **62**, 8). The substance showed two absorption bands, of which that with its maximum at 6150 was broader than that of maximum 5900; the sensitising action was weak, extending to 6900, with a crest at about 5850. Photographs taken under the same conditions with 1:1'-dimethylcarbocyanine iodide proved to be identical in every respect.

When the amounts of methylenediquinaldine dimethiodide and of quinoline ethiodide were kept constant each at 1 mol., while the quantity of alkali was varied, an optimum yield of pure carbocyanine was produced with $2\frac{1}{2}$ mols. of excess sodium. The best yield

(42 per cent.) was, however, obtained with 2 mols. of quinoline alkylhalide to three of sodium, as described above. Nothing was gained by raising the amount of quinoline ethiodide to 3 mols., but if that of the sodium was increased, even by $\frac{1}{2}$ mol., while the quantity of quinoline ethiodide remained stationary at 2 mols., there was a corresponding decrease in the yield; 4 mols. of sodium, in presence of 3 or 4 mols. of quinoline ethiodide, still gave the optimum yield of carboeyanine from methylenediquinaldine dimethiodide. When the filtrate from a preparation, in which insufficient quantities of soda and of quinoline ethiodide had been taken, was subsequently treated with more of these reagents, no further formation of carboeyanine resulted.

In a similar preparation of the dye, quinoline ethiodide was replaced by 6-methylquinoline ethiodide, and from 3 grams of methylenediquinaldine dimethiodide there was obtained 38 per cent. of the theoretical yield of pure carboeyanine (Found: $\text{I} = 27.91$. $\text{C}_{23}\text{H}_{21}\text{N}_3\text{I}$ requires $\text{I} = 28.06$ per cent.). The melting points of this specimen, of dimethylcarboeyanine iodide prepared in the usual way, and of the mixture, were then taken simultaneously and all lay at 284° . The sensitisation spectrograph also showed the substance to be 1:1'-dimethylcarboeyanine iodide.

Preparation of 1:1'-Diethylcarboeyanine Iodide from Methylene-diquinaldine Diethiodide.

One mol. of methylenediquinaldine diethiodide (3.05 grams) and 2 mols. of quinoline methiodide (2.89 grams), dissolved in hot rectified spirit (250 c.c.) with $\frac{1}{2}$ mol. of hydrochloric acid, were treated with $3\frac{1}{2}$ mols. of sodium, dissolved in alcohol. The carboeyanine, which crystallised on cooling, was filtered off and washed with hot alcohol, and the yield of crude product (1.59 grams) was 62 per cent. of the theoretical. On recrystallisation from methyl alcohol the yield of pure dye was 47 per cent. For analysis, it was dried in a vacuum at $120-130^\circ$ until of constant weight (Found: $\text{C} = 62.34$; $\text{H} = 5.40$; $\text{N} = 5.80$; $\text{I} = 26.52$. $\text{C}_{25}\text{H}_{23}\text{N}_3\text{I}$ requires $\text{C} = 62.48$; $\text{H} = 5.25$; $\text{N} = 5.84$; $\text{I} = 26.43$ per cent. Loss on drying = 6.3. $\text{C}_{25}\text{H}_{25}\text{N}_3\text{I} \cdot \text{CH}_3\text{OH}$ requires $\text{CH}_3\text{OH} = 6.3$ per cent.). Its melting point, that of 1:1'-diethylcarboeyanine iodide, and of their mixture, all lay at $287-288^\circ$; melting was in all three cases followed by decomposition. In appearance, the green needles of the substance were exactly like those of 1:1'-diethylcarboeyanine iodide. There were two absorption maxima at 6000 and 5650, respectively, and of these, the former band was the more intense; the compound was an excellent sensitiser, and its action extended to 6950 for moderate exposures and was uniform except for a centre

of depression in the green about 5100. The corresponding spectrographs for 1 : 1'-diethylcarbocyanine iodide were indistinguishable from these.

Preparation of 6 : 6'-Dimethyl-1 : 1'-diethylcarbocyanine Iodide from 6 : 6'-Dimethylmethylenediquinaldine Diethiodide.

A solution of 1 mol. of 6 : 6'-dimethylmethylenediquinaldine diethiodide (3.19 grams) and 2 mols. of quinoline methiodide in rectified spirit (300 c.c.) with $\frac{1}{2}$ mol. of hydrochloric acid was treated with an alcoholic solution of $3\frac{1}{2}$ mols. of sodium. The yield of crude product was 61 per cent. of the theoretical, and after two recrystallisations from methyl alcohol it was 38 per cent. On drying in a vacuum at 120—130°, practically no loss in weight took place (Found : C = 63.83; H = 5.81; N = 5.46; I = 25.16. $C_{27}H_{29}N_2I$ requires C = 63.77; H = 5.75; N = 5.51; I = 24.97 per cent.). The substance showed no sign of melting up to 320°, nor did 6 : 6'-dimethyl-1 : 1'-diethylcarbocyanine iodide, nor a mixture of the two dyes. They were exactly similar in appearance. The compound prepared by this new method gave a band of extra sensitisation which had a very marked crest in the extreme red at 7050 and which fell off very rapidly to zero at 7350; this abrupt decrease in sensitiveness is characteristic of 6 : 6'-dimethyl-1 : 1'-diethylcarbocyanine iodide, and its spectrograph, made for comparison, was found to be identical.

Benzylidenediquinaldine and its Diacid Salts.

Koenig's method of preparing benzylidenediquinaldine was followed (*loc. cit.*). The hydrochloride was found to be not more but less soluble in water than in absolute alcohol containing a little hydrochloric acid; after one recrystallisation from the latter solvent the yield was 55 per cent. of the theoretical. The crude dihydrochloride was yellow, but three extra recrystallisations rendered it absolutely colourless. When heated, shrinking began at 147°; m. p. 154—156°. A specimen for analysis was dried in a vacuum (Found : Cl = 15.85. Calc. for $C_{27}H_{25}N_2Cl_2$, Cl = 15.82 per cent.). This pure product still exhibited a remarkable property which was shown also by the crude substance, namely, where the daylight had failed to penetrate, the mass was pink instead of colourless. The pink tint was instantaneously dispelled on exposure to sunlight, but it redeveloped when the white dihydrochloride was kept in the dark.

Benzylidenediquinaldine dinitrate was much less soluble in hot dilute acid and in water than was the dihydrochloride. The pure dinitrate was crystalline and pale yellow. When heated, it became

sticky at 90° and melted at 100–112°, according to the rate of rise of temperature. It was dried in a vacuum desiccator before analysis (Found: $\text{NO}_3 = 24.97$. $\text{C}_{27}\text{H}_{24}\text{N}_2(\text{NO}_3)_2$ requires $\text{NO}_3 = 24.78$ per cent.).

From its once recrystallised dihydrochloride, beautiful, colourless prisms of benzylidenediquinaldine were obtained by the following method: a slight excess of sodium hydroxide was dropped into a cooled aqueous solution of the salt, and the precipitated base was extracted with ether; after drying the ethereal solution with anhydrous sodium carbonate, most of the solvent was distilled off and the concentrated residue stirred, when crystallisation took place; the benzylidenediquinaldine was usually filtered from the small amount of ethereal solution with which it was in contact, as more soluble impurities were thus removed. For analysis, a specimen was dried over sulphuric acid in a vacuum (Found: $\text{C} = 86.04$; $\text{H} = 5.99$; $\text{N} = 7.37$. $\text{C}_{27}\text{H}_{22}\text{N}_2$ requires $\text{C} = 86.57$; $\text{H} = 5.93$; $\text{N} = 7.49$ per cent.). Crystalline base was also deposited from benzene solution by evaporation of the solvent, and it could be recrystallised from hot acetone. When heated, the above analytically pure specimen melted at 90–94° to a cloudy liquid, which suddenly cleared when the temperature reached 106–107°; its behaviour was due to transformation into a modification of higher melting point, and such a conversion occurred, without melting, when the temperature was slowly raised to 100°. When the original base was more rapidly heated, as by placing it on a boiling-water bath, it gave a cloudy liquid, which gradually cleared and then crystallised on stirring; but if the fluid was allowed to cool to room temperature, the resultant glass was of so great a viscosity that even stirring and inoculation did not cause its crystallisation. The melting point of this second form was 106.5–107.5°. In two experiments, 35 grams of the dihydrochloride gave 22 grams of the base; that is, 75 per cent. of the theoretical yield (Found: $\text{C} = 86.84$; $\text{H} = 6.08$; $\text{N} = 7.37$. $\text{C}_{27}\text{H}_{22}\text{N}_2$ requires $\text{C} = 86.57$; $\text{H} = 5.93$; $\text{N} = 7.49$ per cent.). Thus from the analysis it was concluded that the two substances are isomeric forms of benzylidenediquinaldine, and this was confirmed because the conversion of the first modification into the second was unaccompanied by change in weight. The reverse transformation was effected by dissolving the substance of sharp melting point in absolute ether, for when the solvent evaporated, the form of indefinite melting point was recovered. Specimens of each were converted into dihydrochloride, under identical conditions, and both salts formed the same type of crystals, with the same melting point. The bases behaved alike with methyl iodide.

Preparation of the Methiodides of Benzyldenediquinaldine.

To prepare the dimethiodide of benzyldenediquinaldine, the base (10 grams) was heated with a large excess of methyl iodide (10 c.c.) in a sealed tube at 55–60° for twenty-four hours. To ensure the purity of the product, it was powdered and heated for a further twenty-four hours with the same amount of methyl iodide. After removal of excess of methyl iodide, the solid was extracted with ether in a Soxhlet apparatus. The yield of dimethiodide was 93 per cent. of the theoretical and it was almost pure (Found: I = 38.15 per cent.), but the complete purification was somewhat troublesome. It was boiled twice with small quantities of absolute alcohol, and after this treatment the iodide for analysis was recrystallised twice from ethyl alcohol and dried in a vacuum at 60–70° until of constant weight (Found: C = 52.79; H = 4.33; N = 4.19; I = 38.26. $C_{25}H_{25}N_2I_2$ requires C = 52.89; H = 4.29; N = 4.26; I = 38.57 per cent.). This dimethiodide formed minute, very pale yellow crystals which when heated began to darken at 170° and melted at about 183–200° with much decomposition. It was only slightly soluble in hot alcohol, but readily soluble in chloroform and could be precipitated by the addition of ether. The pure dry dimethiodide appeared quite stable.

Attempts to prepare the monomethiodide of benzyldenediquinaldine by heating the substance with one equivalent of methyl iodide in a sealed tube at 55–60° resulted in the production of dimethiodide together with unchanged base; the compound was eventually obtained in a state of purity by an experiment in which a large excess of methyl iodide was used, and one which would have yielded pure dimethiodide, but for the fact that the temperature of the bath was only 48°. Benzyldenediquinaldine (4 grams) and excess of methyl iodide (4 c.c.) were heated in a sealed tube at 48° for twenty-four hours; the product was powdered and again heated with methyl iodide (6 c.c.) for twenty-four hours. After extraction with ether and recrystallisation from alcohol, the yield of pure product was 76 per cent. It was dried in a vacuum at 60–70° until of constant weight (Found: C = 64.80; H = 4.99; N = 5.31; I = 24.40. $C_{25}H_{25}N_2I$ requires C = 65.10; H = 4.88; N = 5.43; I = 24.59 per cent.). Darkening in colour occurred at about 155° with gradual decomposition from that point; m. p. 170–177°. The monomethiodide formed larger crystals than the dimethiodide and differed from it by its considerably greater solubility in chloroform and in alcohol, and by its insolubility in water, whence addition of water to the alcoholic solution caused its precipitation.

The Action of Water on Benzyldenediquinaldine Dimethiodide.

Benzyldenediquinaldine dimethiodide readily dissolved in hot water, giving a solution with a faint tinge of purple, and, on cooling, large orange crystals separated; analysis showed the percentage of iodine to have dropped by about 2. To investigate the nature of this change, a solution of the dimethiodide (3 grams) in water (135 c.c.) was boiled under reflux for two and a half hours, and the solid which separated on cooling was recrystallised three times. The product (0.9 gram) was in the form of orange needles, which darkened on drying; m. p. 231° – 232° with decomposition. For analysis, a specimen was heated in a vacuum at 60 – 70° , and the results were those required for benzyldenequinaldine methiodide (Found: C = 57.92; H = 4.43; N = 3.81; I = 33.71. $C_{18}H_{16}NI$ requires C = 57.91; H = 4.32; N = 3.76; I = 34.02 per cent.). A specimen of benzyldenequinaldine methiodide, which was prepared for the sake of comparison, melted at the same temperature, and the melting point of the mixture was no lower. The compounds were identical in appearance. It was therefore concluded that, by the action of water, benzyldenediquinaldine dimethiodide is converted into benzyldenequinaldine methiodide.

Benzyldenequinaldine methiodide, for comparison, was obtained by heating benzyldenequinaldine ($1\frac{1}{2}$ grams) and excess of methyl iodide (2 c.c.) in a sealed tube at 63 – 65° for twenty-four hours. After extraction with ether, the residue was recrystallised from water, when the yield was 66 per cent. of the theoretical value. For analysis, the compound was dried in a vacuum at 55 – 65° (Found: I = 33.85 per cent.). The orange crystals melted at 231 – 232° with decomposition.

I am deeply indebted to Dr. W. H. Mills for his advice.

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[Received, November 25th, 1922.]

XXXIII.—*An Examination of the Alleged Antimonious Hydroxides.*

By CHARLES LEA and JOHN KERFOOT WOOD.

IN connexion with work done by the authors on the oxychlorides of antimony, which will form the subject of a separate communication, it became necessary to investigate the action of hydrochloric acid on hydrated antimonious oxide. A search of the literature

disclosed a certain amount of confusion concerning the nature and composition of the latter substance and therefore it was thought desirable to make a few experiments in the hope of obtaining more definite information on the subject; the results obtained in this inquiry form the subject of the present paper.

In the early literature no mention is made of the existence of any definite antimonious hydroxide. Mitscherlich (*J. pr. Chem.*, 1840, **19**, 445), referring to the precipitate obtained in the cold by the action of solutions of sodium carbonate on antimony chloride, states that the precipitate usually changes in the cold, and always on boiling, into a fine powder consisting of small octahedra of the oxide. A statement is, however, met with in some modern works to the effect that, under the conditions specified, a precipitate of definite composition, usually described as metantimonious acid, is obtained. Schaffner (*Annalen*, 1844, **51**, 168) referred to a product which he considered to be pyroantimonious acid, but this was later shown by Serono (*Gazzetta*, 1894, **24**, 274) to consist of orthoantimonious acid. Clarke and Stallo (*Ber.*, 1880, **13**, 1792) claimed to have prepared an orthoantimonious acid by the action of sulphuric acid on barium antimonyl tartrate. The addition of a mineral acid to tartar emetic yielded a product which contained varying amounts of tartaric acid and of the precipitating agent, but Clarke and Stallo stated that the impurities in question could be almost entirely removed by washing. Guntz (*Compt. rend.*, 1886, **102**, 1472) disputed this statement and asserted that even after washing until the wash-water gave no acid reaction the precipitate still contained 5 per cent. of tartaric acid.

Long and Sauer (*J. Amer. Chem. Soc.*, 1891, **17**, 87) also made experiments on the decomposition of tartar emetic solutions, using as precipitants solutions of alkaline carbonates, phosphates, acetates, tungstates, etc. No analyses of the products were given except in the case of that obtained by the use of sodium tungstate, in which case the precipitate was contaminated with tungstic acid and contained antimony varying in amount between 80.2 and 80.9 per cent.; $Sb_2O_3, \frac{1}{2}H_2O$ requires Sb = 80.81 per cent.

Whilst not actually disproving the existence of definite hydroxides of antimony, the experiments made by the authors show that under the conditions specified by Clarke and Stallo the precipitate obtained does not correspond in composition with orthoantimonious acid. The composition of the product obtained by Long's method varies somewhat according to the temperature of preparation; at the ordinary temperature, the composition of the precipitate approximates to $Sb_2O_3, \frac{1}{2}H_2O$.

EXPERIMENTAL.

Action of Acids on Tartar Emetic and Similar Compounds.

With the object of repeating the work of Clarke and Stallo, a quantity of barium antimonyl tartrate was prepared by mixing solutions containing equivalent amounts of tartar emetic and barium chloride. The dried crystalline product was found to contain 19.1 per cent. of barium; barium antimonyl tartrate requires $\text{Ba} = 19.32$ per cent.

An aqueous solution of the barium salt was mixed in the cold with one containing the theoretical amount of sulphuric acid for double decomposition. The filtrate obtained by removal of the barium sulphate was boiled and yielded a white precipitate, which was filtered, thoroughly washed, and air-dried. The amount of antimony present in two separately prepared samples was estimated [Found: (a) $\text{Sb} = 64.2$ per cent., equivalent to $\text{Sb}_2\text{O}_3 + 4.73\text{H}_2\text{O}$; (b) $\text{Sb} = 65.2$ per cent., equivalent to $\text{Sb}_2\text{O}_3 + 4.37\text{H}_2\text{O}$].

Clarke and Stallo stated that their preparation, supposed to have a composition represented by the formula $\text{Sb}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$, was stable at 150° , but on heating sample (a) in a steam-oven until it acquired constant weight it was found that the resulting product had a composition in agreement with the formula $\text{Sb}_2\text{O}_3 \cdot 2.29\text{H}_2\text{O}$.

Sample (b) was unchanged in composition after six months' keeping in a closed bottle.

A solution of tartar emetic was then treated with hydrochloric acid; the resulting precipitate was washed by decantation until it commenced to peptise, when it was filtered, washed with water until the washings gave no reaction for chlorides, and dried on a porous plate until of constant weight. The product contained 66.0 per cent. of antimony, corresponding with a composition of $\text{Sb}_2\text{O}_3 \cdot 4.21\text{H}_2\text{O}$; a similar sample left exposed to air, but protected from dust, was found after six months to have a composition corresponding with $\text{Sb}_2\text{O}_3 \cdot 4.44\text{H}_2\text{O}$.

Another portion of the washed product was kept in contact with a large volume of water for six months. The originally white solid had then assumed a pale buff colour, whilst the supernatant liquid was acid in reaction and gave a white precipitate with silver nitrate insoluble in nitric acid. There was also present a gelatinous product, apparently organic in nature, similar to that frequently observed in solutions of tartaric acid which have been kept for some time. The buff-coloured solid, after washing and drying, contained 82.6 per cent. of antimony; antimonious oxide requires $\text{Sb} = 83.3$ per cent. Under the microscope, the substance was seen to be made up of minute, octahedral crystals; the original dry

powder, however, was absolutely devoid of crystalline character and appeared to consist of minute, translucent globules when examined by means of the microscope, whilst when heated in an ignition tube it became distinctly charred and water was driven off. The original substance, on moistening, was found to have a faintly acid reaction towards litmus paper and to contain a trace of chlorine.

The observations of the authors tend, therefore, to support the views of Guntz rather than those of Clarke and Stallo. Although the hydrated antimonious oxide cannot be freed from tartaric and mineral acids by the ordinary methods of washing, it would appear that these impurities are removed when the substance is left for a long period in contact with a large volume of water, and that during the process of purification the hydrated product undergoes conversion into the anhydrous oxide.

Action of Sodium Carbonate on Tartar Emetic.—According to Long (*loc. cit.*), a hydrated antimonious oxide is formed when tartar emetic is decomposed by solutions of salts having an alkaline reaction. The reaction was studied by the authors under various conditions of temperature, an amount of sodium carbonate somewhat in excess of that theoretically required being added to the tartar emetic solution. When the reaction took place at the temperature of the laboratory the precipitate only appeared after the mixture had stood over-night, but when boiling solutions of the two compounds were mixed an immediate precipitate was obtained. The precipitates were washed several times by decantation and were then filtered and washed very thoroughly in the Büchner funnel; the washed precipitates were dried in the air until of constant weight and were then analysed, the following results being obtained :

(a) Product obtained at room temperature : Sb = 80.85 per cent., corresponding with $\text{Sb}_2\text{O}_3 \cdot 0.49\text{H}_2\text{O}$.

(b) Product obtained at 100° : Sb = 82.87 per cent., corresponding with $\text{Sb}_2\text{O}_3 \cdot 0.09\text{H}_2\text{O}$.

It appears from the above results that the water content of the product is affected by the temperature at which precipitation takes place, and it was accordingly decided to carry out an experiment at 0° in the hope that a hydroxide of definite composition might be obtained. The precipitate obtained was treated in the same way as the previous ones and was found to have a composition corresponding with $\text{Sb}_2\text{O}_3 \cdot 0.63\text{H}_2\text{O}$. Both this product and that obtained at room temperature consisted for the most part of minute, globular particles mixed with a few octahedral crystals; the substance prepared by the interaction of the boiling solutions consisted almost entirely of octahedra.

Action of Alkaline Carbonates and Hydroxides on Antimonious Chloride.—It is stated in some text-books that a precipitate having the composition of metantimonious acid is obtained by the action of alkaline carbonates on solutions of antimonious chloride. On examining this reaction, it was found that a precipitate similar in appearance to that resulting from the addition of acids to tartar emetic was obtained, but this changed after a few minutes into a comparatively dense, cream-coloured powder which, after washing and drying as usual, was found to have a composition corresponding with $\text{Sb}_2\text{O}_3 \cdot 0.45\text{H}_2\text{O}$. The appearance of the substance, when examined microscopically, was similar to that of the product prepared by Long's method.

It had been observed that when solutions of antimonious chloride were titrated with sodium hydroxide the reaction towards its close proceeded very slowly and it was thought this might be due to the acid present in the amorphous precipitate, which was assumed to be an oxychloride, being only slowly removed. It was considered that a more definite end-point might be attained by adding a slight excess of alkali and then titrating back with a standard acid solution. This was actually found to be the case, but the precipitate under these latter conditions changed in a few minutes to a dense cream-coloured powder, whereas when the alkali was added drop by drop to the original solution until a permanent red colour was obtained with phenolphthalein, the precipitate remained quite unaltered in appearance for a considerable period. In spite of the difference in behaviour, the amount of alkali required in the two experiments was the same, thus indicating that the same amount of chlorine had been removed in each case. If, therefore, the original assumption that the amorphous white precipitate consisted of an oxychloride was correct, the cream powder should have a similar composition. In order to test this point, some of the cream-coloured product was filtered, washed with alcohol and ether to avoid hydrolytic decomposition, dried, and analysed. The amount of chlorine found was less than 0.1 per cent., so precluding the possibility of the substance being an oxychloride, whilst the percentage amount of antimony present was 81.0, corresponding with a composition of $\text{Sb}_2\text{O}_3 \cdot 0.45\text{H}_2\text{O}$. On examination under the microscope, it was found to consist of minute, globular particles, and therefore resembled the products obtained by the other methods which have been described. The substance, instead of being an oxychloride, was evidently a hydrated antimonious oxide containing a small amount of adsorbed hydrochloric acid.

The action of ammonia on solutions of antimonious chloride was

also investigated, and it was found possible by this method to prepare antimonious oxide in a slightly hydrated condition and in a very fine state of division. The most satisfactory method of preparation consisted in pouring a solution of antimonious chloride in hydrochloric acid into an excess of a dilute solution of ammonia, the mixture being well stirred during the operation. As a result of this reaction, a white precipitate in a very fine state of division was obtained; it was washed with hot water until the washings gave no reaction either with Nessler's reagent or with a mixture of silver nitrate and nitric acid. When dried at 100° , the product contained 82.16 per cent. of antimony and only a minute trace of chlorine; no evidence of crystalline structure could be detected even when the substance was examined under the high power of the microscope.

Discussion of Results.

The results obtained by the authors appear to be readily explained in terms of the theory advanced by Collins and Wood (T., 1922, 121, 441) in relation to the isomerism of the stannic acids.

When hydrated antimonious oxide is liberated, as by the action of a mineral acid on a solution of tartar emetic, the finely divided precipitate tends to adsorb some of the added acid or some of the liberated tartaric acid, forming an adsorption product in equilibrium with the solution. On removing the supernatant liquid by decantation and replacing it with fresh water, the equilibrium conditions are disturbed, and some of the adsorbed acid is removed; this operation is repeated at each decantation, until eventually it becomes impossible to detect the acid in the solution by the ordinary methods.

The gradual removal of the acid makes possible the commencement of another action. Antimonious oxide is amphoteric in character, but as long as an appreciable quantity of an acid is present the behaviour of the hydrated oxide in an acidic capacity is impossible. As the acid is removed, however, the hydrated oxide begins to act as an acid in addition to behaving as a base; interaction between molecules acting in these two capacities will lead to the formation of a condensation product of a salt-like nature. If the solid is left in contact with water for a considerable period, the last traces of adsorbed acid are slowly removed and the process of condensation continues until an almost anhydrous product is eventually obtained.

Hydrated antimonious oxide is more feeble as an acid than as a base. When, therefore, the substance is precipitated by an alkaline reagent, there is little tendency for the formation of adsorption compounds with the alkali employed; on filtering and washing

the product, therefore, condensation can proceed unchecked and the almost anhydrous oxide is obtained more readily than when an acid precipitant is employed.

The results obtained when a solution of antimonious chloride is titrated with sodium hydroxide may be explained as follows. The precipitate begins to separate before the neutral point is reached and may at this stage be regarded as a hydrated basic chloride. As the addition of the alkali is slowly continued, the chlorine is gradually removed, the removal of the last traces of halogen by the practically neutral solution taking place slowly; the small amount of acid retained by the precipitate makes no appreciable difference to the titration, but retards the process of condensation. If a slight excess of alkali is added, the whole of the halogen is eliminated, condensation can then proceed unhindered, and the nearly anhydrous oxide results.

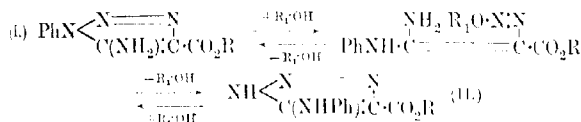
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[Received, November 16th, 1922.]

XXXIV.—2:5-Iminodihydro-1:2:3-triazole. Part I. Constitution of Dimroth's 5-Anilino-1:2:3-triazole.

By PAVITRA KUMAR DUTT.

DIMROTH (*Ber.*, 1902, **35**, 4041; *Annalen*, 1909, **364**, 183) claims to have discovered a peculiar case of isomeric change of the diazo-amine type in connexion with his work on the synthesis of 1:2:3-triazole derivatives. For instance, 5-amino-1-phenyl-1:2:3-triazole-4-carboxylic ester (I), when heated in alcoholic solution with sodium ethoxide, is transformed into an isomeric substance, 5-anilino-1:2:3-triazole-4-carboxylic ester (II). The mechanism of the change, which is reversible, is explained by the author in the following manner:



The same change is brought about by the action of boiling pyridine or by heating the dry substance alone.

The two esters, on hydrolysis, give the two corresponding carboxylic acids. Both, however, give the same acetyl derivative, corresponding to formula II inasmuch as it produces the ester II on being hydrolysed with aqueous alkali.

The two carboxylic acids, when heated, lose carbon dioxide and produce the same substance, m. p. 139°, to which Dimroth ascribes the constitution of 5-anilino-1-phenyl-1:2:3-triazole (III).



Dimroth also prepared an isomeride of this compound, m. p. 110°, in a manner which leaves no doubt as to its constitution (*Annalen*, 1909, **364**, 210). He represents this substance as 5-amino-1-phenyl-1:2:3-triazole (IV).

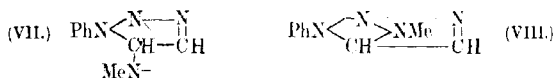
The latter (IV), when heated alone at 145° or boiled with pyridine, is converted into the former (III). The mechanism of the change is, according to Dimroth, the same as that of the ester I into II, and he accounts in a similar way for the conversion of 5-methyl-amino-1-phenyl-1:2:3-triazole (V) into 5-anilino-1-methyl-1:2:3-triazole (VI) by heating with water or pyridine.

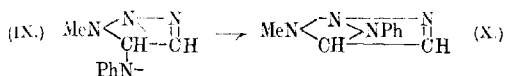


No attempt has been made by Dimroth to elucidate the constitution of what he calls 5-anilino-1-phenyl-1:2:3-triazole (III). The formation of a nitroso-compound is not sufficient proof of its constitution, and one of the objects of this investigation was to find evidence for or against this formula. The conversion of Dimroth's 5-methylamino-1-phenyl-1:2:3-triazole (V) into 5-anilino-1-methyl-1:2:3-triazole (VI), which he regards as a proof of its constitution, merely shows that the mechanism of the isomeric change, whatever it may be, is the same in all three cases.

It appeared to the author that Dimroth's hypothesis is untenable on the ground that the same changes are brought about in a solvent like dry pyridine or by heating the dry substances only. In this paper a simpler explanation of this change is formulated.

Assuming the structure of Dimroth's 5-methylamino-1-phenyl-1:2:3-triazole to be correctly represented by V, it can be easily imagined that under the influence of heat or various reagents the hydrogen atom of the methylamino-group migrates from the nitrogen to the adjacent carbon atom of the triazole ring, the consequent redistribution of the valencies of the different atoms forming part of the ring being represented in VII. Ring closure by union of the free valencies of the nitrogen atoms would immediately ensue and the four-membered ring (VIII) be produced.

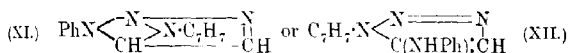




Now from its method of formation, Dimroth's 5-anilino-1-methyltriazole may be regarded as having undergone the same isomeric change (IX \rightarrow X).

On comparing the two formulæ VIII and X, it is easily seen that they represent the same substance. The change of the substance V, m. p. 102°, into the isomeride (X) of m. p. 172° is thus made clear. The constitution of the latter is, however, not thereby proved, for it may be represented by VIII (or X) or by that (VI) of Dimroth's 5-anilino-1-methyltriazole, the hydrogen atom attached to the tertiary carbon atom (formula VIII or X) having wandered to the negatively substituted nitrogen atom with consequent opening of the four-membered ring.

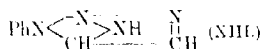
In order to obtain evidence for one or other of these formulæ (VI and VIII), and also in support of the scheme just formulated, two different series of compounds have been made under exactly similar conditions. In one series, 5-hydroxy-1-phenyl-1 : 2 : 3-triazole-4-carboxylic ester (Dimroth, *Ber.*, 1902, **35**, 4040), prepared by condensing phenylazoimide with malonic ester, was converted, by successive treatment with phosphorus pentachloride and with *p*-toluidine, into an ester, the free acid of which, by loss of carbon dioxide, readily gave a substance, m. p. 171—172°, which would, according to the above hypothesis, have the constitution



The substance does not give an acetyl or an *N*-nitroso-derivative and therefore its constitution must be represented by XI.

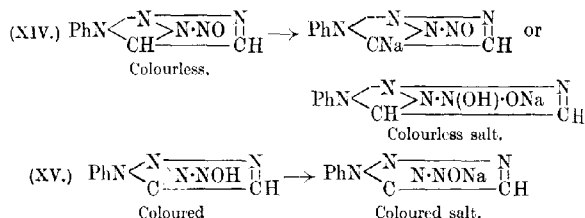
Similarly, in the second series of experiments, starting from *p*-tolylazoimide and malonic ester and going through the same course of reactions but substituting aniline for *p*-toluidine, the free acid obtained yielded, by loss of carbon dioxide, the identical substance (XI), m. p. 171—172°. The constitution given to the substance, and the hypothesis formulated above, may therefore be regarded as established, although the evidence is mainly indirect.

Dimroth's 5-anilino-1-phenyldihydro-1 : 2 : 3-triazole,



This formula accounts for all its properties as yet examined. For example, it gives a colourless mononitroso-compound which

dissolves in alkalis, forming a colourless solution. On keeping, especially in sunlight, and on recrystallisation from alcohol, it changes to a greenish-yellow compound. The latter gives a red solution in alkalis, from which the yellow nitroso-compound is precipitated on the addition of acids. These changes may be represented as follows:

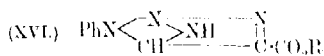


The nitroso-compound, when heated with water or sodium bicarbonate solution, gives the original phenyliminodihydrotriazole (XIII), and when heated with aniline forms the same compound together with aminoazobenzene.

The substance XIII gives a monomethyl (m. p. 198—199°) and a monoacetyl (m. p. 141—141.5°) derivative, as would be expected from its structure. If Dimroth's formula were correct, a disubstituted product should be formed in each case. It should, however, be mentioned that the monomethyl derivative described in this paper differs in its melting point from Dimroth's 5-anilino-1-methyl-triazole (m. p. 172°), and it is hoped that further work will reveal the constitution of the former.

Lastly, the substance XIII is not very stable. Treated with an oxidising agent, it readily decomposes, giving off nitrogen and phenylcarbylamine. Its alcoholic solution gradually decomposes at the ordinary temperature and smells strongly of carbylamine, and the same odour is developed even by the carefully purified, odourless substance, after keeping in a dry bottle for some time. It seems as though the internal strain of the four-membered ring is sufficient to make the whole molecule unstable.

Dimroth's acid ester (II) should, according to the evidence put forward in this paper, be regarded as having the constitution:



It is obvious that the transformation of the ester I into XVI and vice versa by the action of heat or various reagents can also be accounted for by the same scheme as given above (p. 266).

The iminodihydrotriazole derivatives having two different

radicles in the four-membered ring contain an asymmetric carbon atom. Experiments on the resolution of these compounds are in progress.

EXPERIMENTAL.

Phenylazoimide.—The method of preparing aromatic azoimides previously described (T., 1921, 119, 2088) has been modified so that fairly large quantities can be made in a short time and at a reasonable expense. Twenty-eight grams of aniline, dissolved in 90 c.c. of strong hydrochloric acid and 90 c.c. of water, are diazotised with 21 grams of sodium nitrite dissolved in 60 c.c. of water. The diazo-solution is added to a solution of 51 grams of *p*-toluenesulphonamide and 45 grams of sodium hydroxide in 700 c.c. of water at the ordinary temperature. After some time, the mixture is steam-distilled and the azoimide purified in the ordinary way. Yield 26–27 grams.

p-Tolylazoimide.—The same procedure is followed in this case. Forty grams of *p*-toluidine, dissolved in 120 c.c. of strong hydrochloric acid and 90 c.c. of water, are diazotised with 28 grams of sodium nitrite in 60 c.c. of water. The diazo-solution is added to 51 grams of *p*-toluenesulphonamide and 60 grams of sodium hydroxide dissolved in 700 c.c. of water. Yield 31–32 grams.

Ethyl 5-Amino-1-phenyl-1:2:3-triazole-4-carboxylate (Formula I).—A cold solution of 4.6 grams of sodium in 100 c.c. of anhydrous ethyl alcohol is mixed with 22 grams of phenylazoimide, and 22 grams of ethyl cyanoacetate are gradually added with frequent shaking and with external cooling. After leaving over-night, the mixture is diluted with about 600 c.c. of water. The precipitate (yield 29–30 grams; m. p. 125–126°) crystallises from benzene in needles and from alcohol in plates, the melting point remaining unchanged (Found: N = 24.26. Calc., N = 24.13 per cent.). The filtrate and washings, when acidified with concentrated hydrochloric acid, give a crystalline precipitate (prisms) of the free acid, which melts at about 140° with decomposition. Yield 5–6 grams. The crude acid is crystallised from alcohol with charcoal treatment and then melts at 141–142° with decomposition (Found: C = 53.01; H = 4.20; N = 27.65. Calc., C = 52.94; H = 3.92; N = 27.45 per cent.). The same carboxylic acid is obtained by hydrolysing the above ester with aqueous alcoholic sodium hydroxide.

The acetyl derivative of the ester, obtained by boiling it with an equal weight of acetic anhydride for half an hour, separates from spirit in needles, m. p. 103–104° (Found: N = 20.51. Calc., N = 20.44. Dinroth gives m. p. 90° and N = 20.11 per cent.).

Ethyl 2:5-Imino-1-phenyldihydro-1:2:3-triazole-4-carboxylate (XVI).—Thirty grams of the ester I and 70 c.c. of dry pyridine

are heated together under reflux at 150–160° for five to six hours. The mixture is then poured into 500 c.c. of water, cooled, and acidified with hydrochloric acid. The precipitate, which resembles cotton wool in texture and appears under the microscope as a mass of long, hairy crystals, is collected, dissolved in spirit, and the solution treated with a large volume of aqueous sodium carbonate (10 per cent.). A little unchanged insoluble ester having been removed, the filtrate is acidified and the imino-ester (yield 28–29 grams; m. p. 124–126°) recrystallised from dilute alcohol; needles, m. p. 129–130° (Found: N = 24.21 per cent.).

The acetyl derivative of this ester, obtained as in the previous instance, melts at 103–104°, alone or mixed with the acetyl derivative of ester I.

The *methyl* derivative of the ester is prepared by boiling 11.6 grams (1 mol.) of the substance in a solution of 4.6 grams (2 atoms) of sodium in 100 c.c. of anhydrous alcohol together with 30 grams (more than 2 mols.) of methyl iodide until neutral. The alcohol having been distilled off and water added to the residue, the mixture is made slightly alkaline and cooled, and the solid (yield 8 grams) recrystallised from benzene; needles, m. p. 98–99° (Found: N = 23.16. $C_{12}H_{14}O_2N_4$ requires N = 22.76 per cent.). The substance is therefore a monomethyl derivative. Its constitution has not yet been proved. Unlike the parent ester, it does not give phenyl-carbylamine when treated with sodium hypobromite. When hydrolysed with alcoholic sodium hydroxide, it gives the free acid, and the latter on recrystallisation from spirit melts at 222° with decomposition (Found: N = 25.64. $C_{16}H_{18}O_2N_4$ requires N = 25.68 per cent.).

*Conversion of the Imino-ester (XVI) into the Amino-ester (I).—*Ten grams of the ester and 150 c.c. of anhydrous alcohol are heated under reflux while a current of dry hydrogen chloride is passed through for six to seven hours. The alcohol is now distilled off, the residue treated with a large volume of aqueous sodium carbonate (10 per cent.), and the precipitate, after being washed and dried (yield 2.5 grams), recrystallised from benzene. The product melts at 125–126° (Found: N = 24.61 per cent.) and is identical with the ester I. From the filtrate, the imino-ester is obtained on the addition of hydrochloric acid. Dimroth (*Annalen*, 1909, **364**, 205), by heating the substance in alcoholic solution at 150° for three hours, obtained a 23 per cent. conversion into the amino-ester (I), but he did not isolate the product.

Hydrolysis of the Acetyl Derivative of the Ester.—Ten grams of the acetyl compound, dissolved in alcohol, are heated in a current of dry hydrogen chloride as in the previous experiment. After two

hours' heating, the mixture is treated with sodium carbonate solution. A little insoluble matter (0.7 gram) is collected and recrystallised from alcohol. It melts at 124–126° (Found: N = 24.26 per cent.) and is identical with the ester I. The sodium carbonate solution, on the addition of hydrochloric acid, gives a considerable quantity of the ester XVI. The acetyl compound is therefore derived from the latter.

2:5-*Imino-1-phenyldihydro-1:2:3-triazole* (Formula XIII).—Dimroth (*Ber.*, 1902, **35**, 4041) prepared this compound by heating the acid corresponding with the ester I and obtained a yield of 73 per cent. of the crude substance. A better method is as follows: 20.4 grams of the free acid and 50 c.c. of dry pyridine are heated together under reflux at 120–130°. After half an hour, the evolution of carbon dioxide ceases, and after two hours the liquid is poured into 500 c.c. of cold water, acidified with hydrochloric acid, and the solid collected; m. p. 138–139°, yield 14.5 grams (90 per cent.). After recrystallisation from alcoholic solution with charcoal treatment, it is obtained in colourless, rhombic crystals, m. p. 140° (Found: N = 35.15. Calc., N = 35.0 per cent.).

The *picrate*, obtained by mixing alcoholic solutions of the substance and of picric acid, forms needles, m. p. 163° with decomposition (Found: N = 25.53. $C_8H_8N_4 \cdot C_6H_3O_7N_3$ requires N = 25.19 per cent.).

The *acetyl* derivative is obtained by warming the substance with three times the quantity of acetic anhydride on the water-bath until the mixture just begins to darken. Prolonged heating results in decomposition producing a black, sticky mass. The mixture is poured into water, made alkaline with sodium carbonate, and the precipitate crystallised from spirit; needles, m. p. 141–141.5° (Dimroth gives m. p. 137–138°) (Found: N = 28.14. Calc., N = 27.72 per cent.). On hydrolysis with aqueous sodium hydroxide, the original substance (XIII) is obtained.

The *methyl* derivative of the substance (XIII) is obtained in the same way as in the case of methylation of the ester (XVI). It crystallises from absolute alcohol in thick plates and melts at 198–199° (Found: N = 32.32. $C_9H_{10}N_4$ requires N = 32.18 per cent.). Unlike the parent substance, it is insoluble in alkali and does not give carbylamine when treated with alkaline oxidising agents. Its constitution has not yet been proved.

Nitroso-derivative of the Base XIII.—Ten grams of the freshly purified base, dissolved in 400 c.c. of dilute hydrochloric acid (10 per cent.), are treated at 5° with 5 grams of sodium nitrite, dissolved in 100 c.c. of water. The colourless precipitate is washed with ice-cold dilute hydrochloric acid and with ice-water and dried in a

vacuum desiccator in the dark. Yield 11 grams. It melts with decomposition at $117-118^{\circ}$ (Dimroth gives m. p. $115-116^{\circ}$) (Found : N = 37.6. Calc., N = 37.03 per cent.). It dissolves in dilute sodium hydroxide solution in the cold, forming a colourless solution, which when warmed gradually turns red and decomposes. On prolonged exposure to sunlight, the colourless solid turns greenish-yellow and then gives a red solution in alkali. When recrystallised from cold alcohol, the coloured crystals are obtained. Both substances give Liebermann's nitroso-reaction.

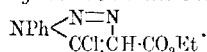
The nitroso-compound is insoluble in sodium bicarbonate solution in the cold and when heated gradually dissolves with partial decomposition (smell of carbylamine). The precipitate obtained on acidifying the clear solution melts at $139-140^{\circ}$ after recrystallisation from alcohol and is identical with the parent substance (XIII) from which the nitroso-compound is derived. The same change occurs when a suspension of the nitroso-compound in water is heated.

Action of Aniline on the Nitroso-compound (XIV or XV).—Five grams of the nitroso-compound are heated with 10 c.c. of aniline on the water-bath for about two hours, the aniline is distilled off in steam, and the residue extracted with hot water and filtered. Crystals appear when the filtrate is cooled. These are filtered off and the clear filtrate used again for extracting the above residue. The total crop of crystals is then thoroughly dried and exhaustively extracted in a Soxhlet apparatus with light petroleum. The extract deposits a reddish-brown, crystalline substance which melts at $124-126^{\circ}$ and is aminoazobenzene (Found : N = 21.51 per cent.). The insoluble residue remaining in the Soxhlet is dissolved in alcohol, decolorised by boiling with animal charcoal, and crystallised. Colourless crystals are obtained which melt at $139-140^{\circ}$, alone or mixed with the substance XIII (Found : N = 35.2 per cent.).

Ethyl 5-Hydroxy-1-phenyl-1:2:3-triazole-4-carboxylate.—A cold solution of 9.5 grams of sodium in 125 c.c. of anhydrous alcohol is mixed with 50 grams of phenylazoimide, and 70 grams of ethyl malonate are added gradually with shaking and cooling. The mixture having been heated under reflux for about two hours, the alcohol and unchanged azoimide are distilled off in steam, and the hot aqueous solution of the residue filtered. On acidifying the filtrate with hydrochloric acid, a semi-solid mass separates which solidifies on cooling. It is filtered, washed, and dried. Yield 70–75 grams. On recrystallising from spirit, the ester separates in yellow prisms, m. p. $72-73^{\circ}$ (Found : N = 18.34. $C_{11}H_{11}O_3N_3$ requires N = 18.02 per cent.).

Ethyl 5-Hydroxy-1-p-tolyl-1:2:3-triazole-4-carboxylate is made in the same way as the preceding ester. Using 9 grams of sodium, 125 c.c. of anhydrous alcohol, 45 grams of *p*-tolylazoimide, and 56 grams of malonic ester, 65–70 grams of the crude ester are obtained. It crystallises from spirit in dull yellow prisms, m. p. 98–99° (Found: N = 17.13. $C_{12}H_{13}O_3N_3$ requires N = 17.0 per cent.).

Ethyl 5-Chloro-1-phenyl-1:2:3-triazole-4-carboxylate,



—Thirty-four grams of the hydroxy-ester and 40 grams of phosphorus pentachloride are heated together on a gently boiling water-bath under reflux for about an hour and a half. It is well to add the phosphorus pentachloride in several portions by momentarily disconnecting the flask, as otherwise the reaction is likely to become too vigorous. The phosphoryl chloride is then distilled off in a vacuum from a water-bath, and the residue dissolved in ether. The ethereal solution is washed several times with water, the ether distilled off, and the residue crystallised from methyl alcohol; colourless needles, m. p. 80–81° (Found: N = 17.09. Calc., N = 16.7 per cent.). The same substance is obtained by the action of nitrous acid on the ester I, dissolved in concentrated hydrochloric acid (Dimroth, *Annalen*, 1909, **364**, 212).

Ethyl 5-Chloro-1-p-tolyl-1:2:3-triazole-4-carboxylate.—This substance is made in the same way as the preceding. It crystallises from absolute alcohol in colourless prisms, m. p. 61–62° (Found: N = 16.07. $C_{13}H_{13}O_2N_3\text{Cl}$ requires N = 15.81 per cent.). Using 35 grams of the hydroxy-ester and 45 grams of phosphorus pentachloride, about 12 grams of the pure chloro-derivative are usually obtained and a little more can be recovered from the mother-liquor.

Action of p-Toluidine on Ethyl 5-Chloro-1-phenyltriazole-4-carboxylate.—Forty grams of *p*-toluidine and 25 grams of the ester are heated together on a water-bath for five to six hours. The excess of *p*-toluidine is then distilled off with steam, the residue dissolved in ether, the ethereal solution washed several times with water, and the ether distilled off. The residue, which consists of ethyl 2:5-*p*-tolylimino-1-phenyldihydro-1:2:3-triazole-4-carboxylate, is hydrolysed with alcoholic potassium hydroxide. The aqueous alkaline solution of the free acid is saturated with carbon dioxide, decolorised by treatment with animal charcoal, and filtered. On adding hydrochloric acid to the cooled filtrate, a colourless precipitate of the free acid is obtained, m. p. 84–87° with decomposition; yield about 25 grams. Its alcoholic solution, when warmed on the water-bath, gradually evolves carbon dioxide,

forming the substance XI, which is, however, best obtained by heating the free acid in a paraffin-bath at 150—160°. When no more carbon dioxide is given off, the residual mass is dissolved in hot alcohol, decolorised, and allowed to crystallise. It forms elongated plates or needles which are colourless with a silvery lustre, and melts at 171—172° (Found: C = 71.6; H = 6.0; N = 22.6. $C_{15}H_{14}N_4$ requires C = 72.0; H = 5.6; N = 22.4 per cent.). 2:5-p-Tolylimino-1-phenyldihydro-1:2:3-triazole is a neutral substance, insoluble in hydrochloric acid or sodium hydroxide solution. It is soluble in glacial acetic acid, from which it crystallises well, and does not react with acetic anhydride even on prolonged boiling.

Action of Nitrous Acid on XI.—1.3 Grams of the substance, dissolved in 25 c.c. of glacial acetic acid, are mixed with 10 c.c. of dilute hydrochloric acid (10 per cent.), and treated with 2 c.c. of 25 per cent. solution of sodium nitrite. The nitrous acid acts very sluggishly and the mixture gradually turns yellow. After eight hours, the clear solution is poured into 400 c.c. of cold water. The yellowish-orange gummy mass that separates is filtered, washed with water (yield 1.2 grams), dissolved in spirit, and water added in small quantities, when an emulsion is formed from which orange prisms are obtained. These melt indefinitely at 135—140°. The percentage of nitrogen in various crops of crystals varies from 23.2 to 23.5. The nitrogen content for a mononitroso-compound should be 25.09 per cent. As the substance does not give Liebermann's nitroso-reaction, it cannot be the N-nitroso-derivative. The nitrous acid must have reacted in a way which is at present inexplicable.

Action of Aniline on Ethyl 5-Chloro-1-p-tolyltriazole-4-carboxylate.—Forty grams of aniline and 26.6 grams of the ester are heated together on a water-bath for five to six hours and the resulting mass is treated as described above (p. 273). The crude free acid usually amounts to about 25 grams and melts with decomposition at 76—81°. When heated in a paraffin-bath as before, it loses carbon dioxide, and the product on recrystallisation from alcohol melts at 171—172°, alone or mixed with the substance XI. Both have the same crystalline form and behave exactly alike with various reagents.

In conclusion, the author wishes to thank Professor J. B. Cohen, F.R.S., for criticism and encouragement, and the Research Fund Committee of the Chemical Society for a grant which has partly defrayed the expenses of this investigation.

THE ORGANIC CHEMICAL LABORATORIES,
THE UNIVERSITY, LEEDS.

[Received, October 26th, 1922.]

XXXV.—*The Absorption of Moisture by Coal (and other Fuels). Part I. A Relation between Degree of Humidity in the Air and Moisture Content of Coal.*

By BURROWS MOORE and FRANK STURDY SINNATT.

It has been known for many years that samples of coal, on exposure to air, after the initial rapid evolution of occluded gases has subsided, gain or lose weight according as the condition of the coal is dry or wet relative to the surrounding air (see N. W. Lord, "Experimental Work of U.S.A. Fuel-testing Plant," 1907; W. A. Bone, "Coal and its Scientific Uses," 1918; V. B. Lewis, "Carbonisation of Coal," 1918; J. S. S. Brame, "Fuel," 1914).

A review of recent investigations shows that comparatively little information has been published as to (1) what extent the variation in weight is associated with the variation in degree of humidity of the surrounding air, (2) the relation of the variation of the moisture content in the air to the variation of "loosely combined moisture" in the coal, (3) what extent, if any, the absorption of moisture and of oxygen influence one another.

Published literature indicates that most investigators, in attempting to obtain a proportionate estimate of the various effects and reactions associated with the "weathering" of coals, have concentrated their attention, in particular, on the capacity of coals to absorb oxygen. Most of the experiments of other investigators with coals in a fine state of division appear to have been made on samples of considerable weight and at temperatures higher than normal atmospheric temperature. In the present investigations it was decided to conduct all experiments at the temperature of the air in the laboratory and to use samples of fuel in the form of thin layers in order to minimise the effect of incomplete or uneven absorption and to emphasise the influence of size of the particles.

EXPERIMENTAL.

The experiments were made on samples of Wigan Arley, Wigan Yard, anthracite, Indian coal, gas coke, and Irish peat, which had been stored for some months after being mined. About 3 grams—sufficient to cover the bottom of shallow glass dishes ($2\frac{1}{2}$ inches in diameter) as a thin layer—of the samples, ground to pass a 200×200 mesh sieve, were heated for one hour in an oven at 105° , cooled over concentrated sulphuric acid in desiccators, and weighed. They were then exposed to the air of the laboratory.

Each dish was placed on a central support of height 1 inch, this support being surrounded by four others of height $\frac{3}{4}$ inch. A glass dish 4 inches in diameter was inverted over the sample so as to rest on the small supports. This arrangement was adopted in order to protect the sample from dirt, etc., during exposure to the air of the laboratory.

The variation of humidity in the air was recorded by a wet and dry bulb hygrometer, suspended in the air immediately surrounding the samples. The temperature of the air was recorded. Readings of the hygrometer and the thermometer were noted immediately before the samples were weighed, this being done at definite intervals of time during a period of about one thousand hours. Curves were constructed by plotting values of degree of humidity and of percentage increase of weight at the same intervals of time. The curves were so drawn that the slope at any point would represent the rate of change of the degree of humidity or the rate of change of the percentage increase of weight. In the case of the samples of Wigan Yard, anthracite, Indian coal, gas coke, and Irish peat, the results are represented graphically for two separate periods, (1) from the moment of exposure to the four hundredth hour, (2) from the five hundred and eightieth hour to the nine hundred and eightieth hour. It was considered of interest to ascertain the difference, if any, between the curves during the first and the second periods.

Discussion.

The steepness of the slopes of the curves of percentage increase of weight for the first 24 hours, as compared with that of the humidity curve, suggested that during this period either (1) the absorptive capacity of the coal for moisture is so great that a considerable variation in the humidity of the air appreciably affects neither the rate of absorption of moisture nor the quantity absorbed, or (2) the rapid increase of weight is mainly due to absorption and dissolution of oxygen. After the first twenty-four hours' exposure, the samples seem to become more or less saturated with physically and chemically absorbed moisture, oxygen, and other gases from the air, and so soon as the initial "fresh" reactive condition is passed the variation in weight seems proportional to that of the degree of humidity, suggesting that the gain or loss of weight is now due chiefly to gain or loss of moisture, some of which at least seems to be loosely attached to the still permeable or porous sample of fuel.

A further analysis of the curves in the case of the Arley and anthracite samples—by plotting values of percentage increase

of weight against corresponding values of degree of humidity (Figs. 3 and 4)—shows that during the particular periods of exposure the points plotted lie very nearly on a smoothed curve. It will

FIG. 1.

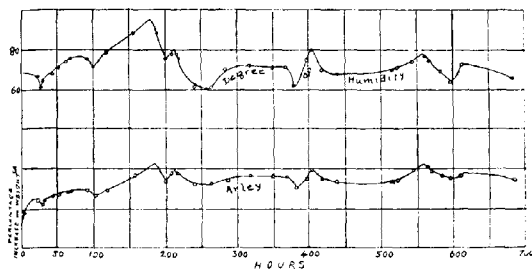
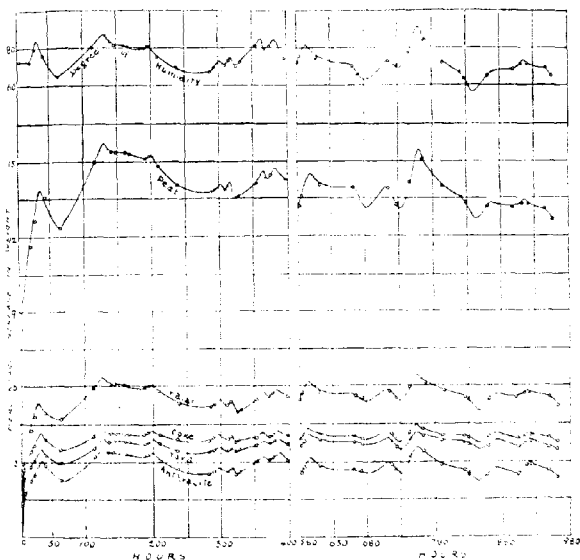


FIG. 2.



be seen that in both cases the smoothed curve for the first twenty-four hours of exposure is approximately parabolic; from the twenty-fourth hour there appears to be a definite qualitative relation

L*

between degree of humidity and percentage increase of weight, although the rate of the average increase of weight is not constant throughout the whole period of exposure.

The curves (Fig. 2) of the other fuel samples examined indicate that in these cases a similar relation exists.

It is concluded that from about the twenty-four hour of exposure the relation between degree of humidity and percentage increase of

FIG. 3.

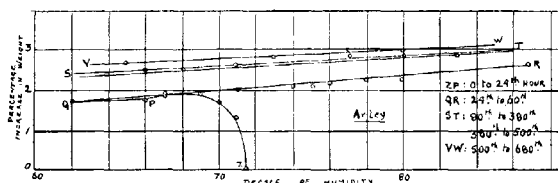
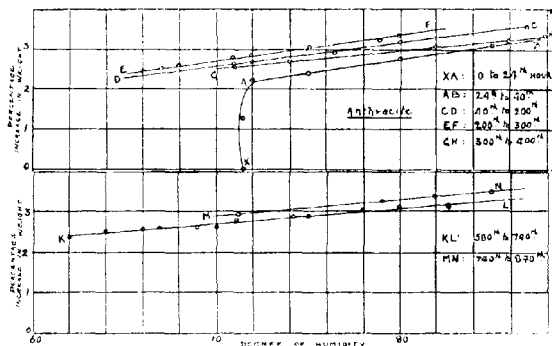


FIG. 4.



weight is capable of being represented approximately by a simple formula, and would indicate the existence of certain constants—specific of the various fuels—by means of which the moisture content of a fuel could be approximately calculated from the degree of humidity of the air surrounding it.

The relation between increase of weight of a fuel and degree of humidity of the air disclosed by the curves precludes the probability that absorption of oxygen increases with decreasing absorption of moisture and suggests that the effect of oxidation is practically negligible.

The results described in the present paper, and others to be published later, appear to furnish evidence of the colloidal nature of coal; and it would seem that the method described here might be applied to the differentiation of the colloidal nature of coals and their constituents as well as to the characterisation of the different types.

It is suggested that the transitional changes which occur in the formation of coal seams may be accompanied by an alteration in the colloidal nature of the changing material.

Summary.

(1) The rate of absorption of oxygen by a fuel decreases until after the first twenty-four hours' exposure it is so slow that variations in humidity produce proportionate variations in the increase of weight of the fuel.

(2) After about the twenty-fourth hour of exposure, a close relation exists between increase of weight and degree of humidity; such relation being representable by a simple formula and suggesting the existence of constants—specific to the type of fuel examined—by which the approximate moisture content might be determined by simple calculation.

(3) No relationship appears to exist between variation in the absorption of moisture and absorption of oxygen.

(4) The fact that the moisture content of coal undergoes rapid variations is of importance in the preservation of samples for analysis.

(5) The variation in moisture content may have an unsuspected influence on the degree of inflammability of coal dust.

The authors wish to express their thanks to the Department of Scientific and Industrial Research for a grant to one of them which partly defrayed the cost of the investigation; acknowledgment is also due to the Lancashire and Cheshire Coal Research Association for supplying the samples of fuel used.

THE COLLEGE OF TECHNOLOGY,
MANCHESTER.

[Received, November 28th, 1922.]

The Metallurgical Applications of Physical Chemistry.

A LECTURE DELIVERED BEFORE THE CHEMICAL SOCIETY ON
DECEMBER 14TH, 1922.

By CECIL HENRY DESCH.

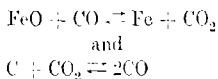
HISTORIANS of science have recognised the debt that chemistry owes to the practical metal smelter and refiner. Centuries of experience in the extraction of metals from their ores and in the removal of impurities by refining led to the accumulation of a vast store of facts, on which the scientific chemist could draw at need, and studies of the behaviour of metals are prominent in the work of most of the founders of chemistry, Boyle, Mayow, Priestley, and Lavoisier. In more recent times the debt is being repaid, the practical metallurgist making use of the knowledge gained by the scientific chemist to improve his processes or to devise new ones, to remove harmful impurities, or to modify the properties of metals by the formation of new alloys. Metallurgical science is an application of physics and chemistry to the special case of the metals, and the corresponding art is founded, more and more deliberately as industry advances, on the science.

It is in the domain of physical chemistry that applications of known scientific principles to metallurgy have been most fruitfully made. On the other hand, the physical chemist has a rich field for study in the ascertained facts of metallurgical experience, a field in which ample opportunity may be found for verifying theoretical conclusions by the observation of technical processes. This is nowhere more conspicuous than in the study of chemical equilibria, since most processes in the smelting of metals depend on balanced reactions. The application is not always easy, for the number of components of a system may be large, whilst heterogeneous systems are commonly involved, solids, liquids, and gases being concerned at once in the reaction. In such cases, as is well known, it is difficult to ensure equilibrium, especially when some of the reacting substances are solid. This is true even in laboratory experiments, but on the large scale, when the gases pass through the reaction vessel with a certain velocity, the difficulty becomes more acute. At the high temperatures usually involved, however, the departure from equilibrium is sometimes quite small.

As an example of such reactions, the roasting of a sulphide ore by heating in air may be taken. The sulphide is heated to a temperature well below its melting point, and the products are the oxide and the sulphate together with sulphur dioxide, the reactions being reversible. The conditions under which the one or the other

solid product may be formed have been determined, and on the proper control of the roasting conditions depends the success of the process. Thus, in preparing a zinc ore for the distillation process, the removal of sulphur must be as complete as possible, and the formation of sulphates is, therefore, to be avoided, whilst in an old process for separating silver from copper the former is converted into sulphate at a temperature at which copper sulphate is completely decomposed, forming the oxide. In such cases, no doubt, the practical discovery of the approximately correct conditions has preceded the theoretical study, but where economical working depends on obtaining the maximum yield of a given product, the careful study of diagrams showing the relations between pressure, temperature, and composition often makes it possible to obtain a higher efficiency.

The best known example of a process of this kind, which has found its way into the ordinary class books, is the reduction of iron ore in the blast furnace. This was probably also the first case to be studied scientifically. The famous memoir of Bunsen and Playfair in 1845, extended by the important treatise of Lowthian Bell in 1872, laid the foundations of our knowledge of the reactions occurring in the blast furnace, whilst later workers, mostly in Germany, have made laboratory experiments for the purpose of determining the conditions of equilibrium. At first sight, the problem is a relatively simple one, since the only elements involved are iron, oxygen, and carbon. The two fundamental reactions are :

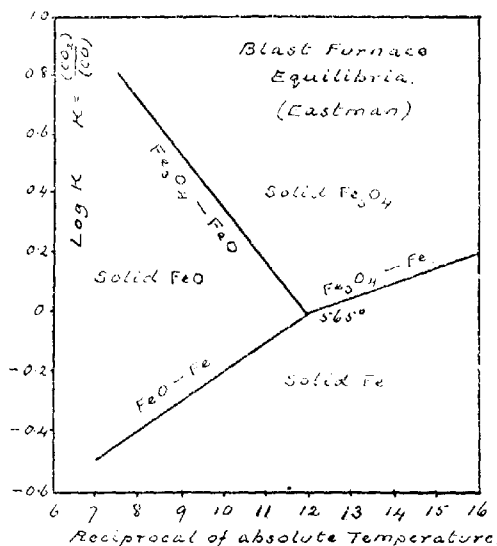


iron behaving as a catalyst towards the second reaction, but Fe_3O_4 can also be in equilibrium with FeO and with iron, and there is the further complication that solid solutions can be formed to a limited extent between the oxides, and that iron can dissolve both oxygen and carbon. It is probably unnecessary to assume, as Schenck has done, reactions leading to the formation of the carbide Fe_3C , which is not stable within the range of temperature considered, but the iron undoubtedly takes up carbon in the solid state, and more rapidly when the melting point of the eutectic is reached. The experimental work on this subject, on which many diagrams have been based, is all open to objection on one ground or another, and the established facts, as far as the solid phases are concerned, are best represented by a diagram due to Eastman,* in which the logarithm of the ratio $K = [\text{CO}_2]/[\text{CO}]$ is plotted against the

* E. D. Eastman, *J. Amer. Chem. Soc.*, 1922, **44**, 975.

reciprocal of the absolute temperature, giving linear relations (Fig. 1). The observed points lie very closely to the three lines shown. The iron ore may enter the furnace as ferric oxide, but reduction to a lower oxide occurs relatively high up in the shaft and need not be considered in the equilibrium. Failure to understand the reversibility of these reactions has led to expensive failures on the large scale. In the hope of converting the whole of the carbon to the dioxide, some ironmasters at one time increased the height of their furnaces, without obtaining the desired result.

FIG. 1.



The ratio of carbon monoxide to dioxide in the escaping gases is determined by the reversibility of the two reactions mentioned above. In spite of its apparent crudeness, the blast furnace has a remarkably high efficiency, both thermal and chemical, provided that the works are so designed as to utilise fully the heating value of the gas which is produced in such enormous volume.

There is another product of the blast furnace of great practical importance and scientific interest, namely, the slag. The solid impurities of the ore and coke must be removed in a liquid form, in order that the iron may be separated from them. It is the temperature at which the slag becomes sufficiently fluid to run

freely that determines the working temperature of the furnace, since the slag is less fusible than the pig iron. Essentially blast furnace slags are composed of silica, lime, and alumina, all the other constituents being of secondary importance as regards fusibility. Any change in the character of the ore means a change in the composition of the slag, and it is evidently impossible to predict, without definite knowledge, whether the change will increase or diminish the fusibility. Actually the melting-point diagram of this ternary system has been most completely worked out by the staff of the Geophysical Laboratory at Washington.* There is, however, a striking peculiarity of molten silicates that affects the practical use of such a diagram. All such mixtures, especially when rich in silica, are extremely viscous immediately above their melting points, so that they are unable to flow freely. The viscosity of slags at various temperatures has been determined in the laboratory of the U.S. Bureau of Mines,† by measuring the torque produced in a graphite cylinder immersed in the molten slag, when the cylindrical containing vessel is rotated. The viscosity falls off rapidly at first with increasing temperature, then more slowly. The reciprocal of the viscosity, or the fluidity, is almost exactly proportional to the temperature. In this way the fluidity of the ternary mixtures has been determined over the required range. The practical value of such knowledge is very great. A furnace using hæmatite may make only 10 cwt. of slag for every ton of iron, whilst with the poor ores of the Midlands as much as 30 cwt. may be produced. During the war many ironmasters accustomed to rich hæmatite ores found their supplies cut off, and were compelled to use the relatively poor Northamptonshire or Lincolnshire ores, with consequent difficulty in determining the conditions of the slag. The use of ternary diagrams was found by the more scientifically minded furnace managers to enable them to control their slags quite satisfactorily.

The importance of slags in the steel industry is at least as great as in iron-smelting. In the open-hearth process the liquid metal is completely covered with a layer of molten slag. Through this layer all the heat for the chemical reactions, radiated from the flames and from the roof, has to pass, and through it the oxygen needed to oxidise the impurities of the pig iron also passes. This oxygen comes in part from the oxidising gases in the furnace and in part from iron oxide added during the working of the charge. It is only in the form of oxides dissolved in the slag that oxygen

* G. A. Rankin and F. E. Wright, *Amer. J. Sci.*, 1915, **iv**, 39, 1.

† A. L. Feild and P. H. Royster, *U.S. Bureau Mines Tech. Paper* 187, 1918; also A. L. Feild, *Trans. Faraday Soc.*, 1917, **13**, 3.

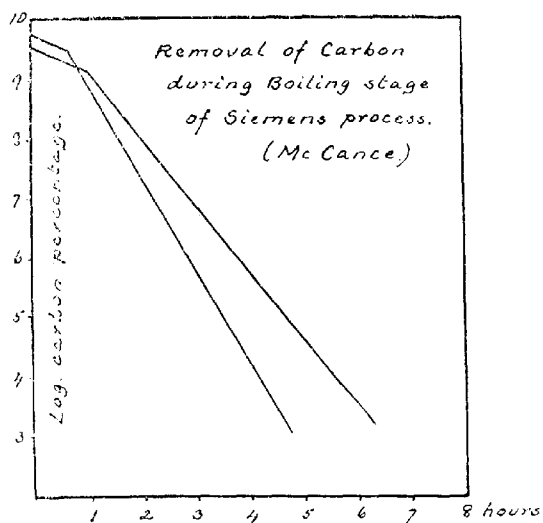
can reach the metal. There is contact between slag and metal, increased as the action becomes violent, when particles of metal are projected into the slag, and particles of slag are entangled and carried down into the steel, but the evidence goes to show that the action is by no means confined to the surface of contact, and that solution and diffusion play their part. The active substance is ferrous oxide, which has a very high solubility in slag and a small, but definite, solubility in molten steel. At a given temperature, therefore, there is a definite ratio between the concentrations of ferrous oxide in the slag and the metal. It is the oxide dissolved in the metal that brings about the oxidation of the silicon, manganese, and carbon in the iron, and as ferrous oxide disappears in these reactions, a further quantity is supplied from the slag. When ore is added, it dissolves, mainly as the magnetic oxide, and the ferrous oxide then distributes itself between slag and metal until equilibrium is reached. The oxidation of the carbon is represented by the reaction $\text{FeO} + \text{C} \rightleftharpoons \text{Fe} + \text{CO}$. The mass of the iron, being very large, may be regarded as constant. The carbon monoxide is evolved as gas, causing the "boiling" of the bath. As at this stage the metal is saturated with gas, the concentration of the carbon monoxide may also be regarded as constant. McCance has shown * by analyses of two open-hearth charges during the boiling stage that, provided that no ore is added, the carbon content of the steel decreases at such a rate that the logarithm of the carbon percentage, plotted against the time, gives a straight line (Fig. 2). The initial straight portion of the graph, meeting the principal line at an angle, corresponds with a stage during which silicon and manganese are still being oxidised as well as carbon, so that the rate of disappearance of carbon is less than it becomes later. Equilibrium is reached, or nearly so, in the later stage, when the steel contains both carbon and oxide in solution. Heat is absorbed in the reaction $\text{FeO} + \text{C} = \text{Fe} + \text{CO}$, and therefore an increase of temperature means a reduction in the quantity of ferrous oxide under conditions of equilibrium. McCance has calculated, by applying Nernst's theorem and using constants which are known with fair accuracy, that an increase of temperature from 1550° to 1600° lessens the quantity of ferrous oxide in solution when equilibrium is reached by one-third.

The slag floats on the steel as oil floats on water, and there necessarily exists an interfacial tension at the bounding surface. As the composition of the liquids changes in consequence of chemical reactions, the value of the interfacial tension also changes, and these alterations, which have not yet been quantitatively studied,

A. McCance, *Trans. Faraday Soc.*, 1918, 14, 213.

are well appreciated by workmen who know nothing of capillary forces, but who can recognise a given surface with accuracy. Cosmo Johns has shown how the workmen's observations may be interpreted in terms of surface tension.* Samples of metal and slag are removed from time to time in a spoon, and are allowed to solidify. On separating the two substances, a clean upper surface of the steel sample may be seen if care has been taken. While the carbon is high, this surface shows dendritic crystals in relief. As the carbon content falls, these crystals are smoothed out more

FIG. 2.



and more completely by the surface forces, and a smooth, bright surface may be obtained. At a later stage, the surface becomes finely wrinkled. The changes in the surface tension of the steel follow closely the changes in its composition, so that an experienced man can infer the one from the other.

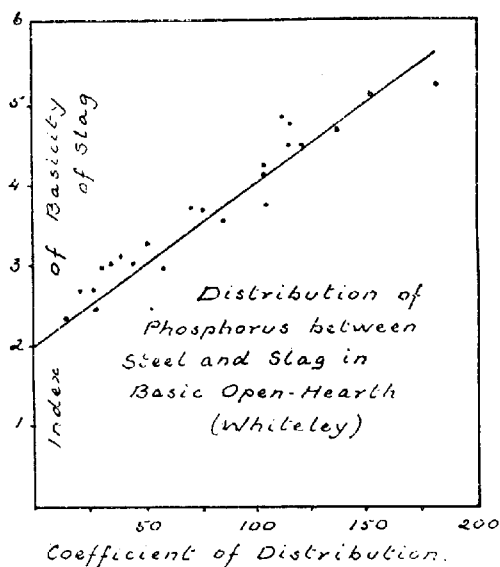
Another application of the principle of distribution of a substance between two solvents to the metallurgy of steel has been made recently by J. H. Whiteley.† In the basic open-hearth process, the removal of phosphorus from steel is known to depend on the

* *J. West Scot. Iron Steel Inst.*, 1919, 26, 36.

† *Proc. Cleveland Inst. Eng.*, 1923.

ratio of bases to silica in the slag. When, in any slag, sufficient lime has been deducted from the analysis to convert all the phosphorus into a stable phosphate, the molecular ratio of the remaining bases to the silica may be calculated and called the index of basicity of that slag. In any charge, the phosphorus is distributed between slag and steel, when equilibrium has been reached, in a definite ratio, so that we may speak of a factor of distribution for phosphorus. Whiteley finds that, when the index of basicity of a number of slags is plotted against this factor of distribution, a straight line

FIG. 3.



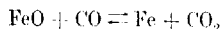
is obtained (Fig. 3), so that the percentage of phosphorus in a steel may be determined, with considerable accuracy, from an analysis of the final or "finishing" slag. The factor is practically independent of the volume of slag, and the proportion of phosphorus in a basic steel may therefore be diminished without any change in the chemical conditions by increasing the volume of slag.

Molten steel, when tapped from the furnace, whatever process has been used in its manufacture, contains a comparatively large volume of dissolved gases, mainly hydrogen and the two oxides of carbon. The solubility of gases in metals has been studied by

Sieverts and his fellow-workers, and has been found to increase as the temperature rises and to be much greater in the liquid than in the solid state. The solubility curve of carbon monoxide in iron has not been determined, but in all probability it is similar in character to the solubility of hydrogen in the same metal, which is known.* As the solubility is found in all cases to be proportional to the square root of the pressure instead of to the pressure itself, it would seem that the gases undergo dissociation in dissolving.

On account of the greatly diminished solubility of gases in solid metals, most of the gas dissolved in molten steel must be released during freezing. A part escapes freely, rising through the liquid, but another part may be entangled between the growing crystals. In this way the cavities known as blowholes are formed, but even when the formation of visible blowholes has been avoided, microscopical observation of sections through ingots shows films of gas separating the individual crystals. The separated surfaces usually unite by welding when the ingot is forged.

The most interesting fact in this connexion is the dependence of the quantity of gas liberated during the freezing of steel on the quantity of oxide dissolved in that steel at the time of tapping. The reaction



is reversible, so that when equilibrium is reached $K = [\text{CO}_2]/[\text{FeO}][\text{CO}]$. When the steel contains much ferrous oxide, the ratio CO_2/CO will be large. McCance has shown† that the known facts may be accounted for by the assumption, highly probable in itself, that solid steel has a much greater solubility for carbon monoxide than for the dioxide, so that when the gases dissolved in the liquid contain much carbon dioxide, blowholes will be formed. A steel containing oxide is, therefore, likely to give unsound ingots or castings. The total quantity of gas in a solid steel is much the same, whether oxide was present or not, but unsound steel, in accordance with the theory, always shows a high ratio of carbon dioxide to monoxide. The importance of deoxidising steel as completely as possible is recognised, but the persistence with which steel can retain oxide is very remarkable. There is evidence to show that the reactions of ferrous oxide, not only with carbon, but also with the other oxidisable elements silicon and manganese, demand an appreciable time for completion, so that reactions may continue in the liquid steel for some time after casting.

In the final casting of the steel into ingot form it is usually necessary to add a small quantity of aluminium, that metal having a remarkable power of preventing the formation of blowholes, a

* A. Sieverts, *Z. physikal. Chem.*, 1911, **77**, 591.

† *Loc. cit.*

power undoubtedly depending on the rapidity and completeness of the removal of the oxide. Of two ingots cast from the same mass of liquid steel, one with and the other without the addition of aluminium, the latter may occupy a very much greater volume than the former, although containing the same weight of steel, the reason being seen when the ingots are sawn through, the one proving to be sound and the other honeycombed with blowholes.

The smelting and refining of metals form only one branch of the art of metallurgy. Another branch is concerned with the preparation of alloys and with the production of a given set of physical and mechanical properties either by alloying with other metals, or by producing changes of structure by thermal treatment or by deformation. In this field the influence of physical chemistry has been more conspicuous, most important industrial advances having been made consciously under scientific guidance. It is here that such striking practical use has been made of new scientific ideas, the application often following rapidly on the heels of the discovery, whether in pure physics or in physical chemistry. The theory of electrolytes, which occupies such a conspicuous place in modern physical chemistry, has few metallurgical applications, since molten metals and alloys do not conduct electrolytically, and it is only in the still obscure field of study of corrosion that electro-chemical theories are invoked. Electro-metallurgy may be regarded as an entirely distinct study.

Both modes of approach to the solution of problems in physical chemistry, the atomic and the thermodynamical, find their uses in metallurgy, but it is the atomic conception that has proved the more useful up to the present, although the more abstract method is now being applied, and may soon prove its value. One of the most notable directions of advance has been in the study of crystalline structure. Metals and alloys are crystalline substances, and their properties depend, therefore, on the arrangement of their component atoms in a space-lattice as well as on their chemical character. The analysis of crystal structure by means of X-rays has been applied to metals by W. H. and W. L. Bragg, Hull, Debye, and others with striking and gratifying results. The form and dimensions of the space-lattice are known accurately for most of the ordinary metals, and the method is now being applied to alloys. We may confidently hope that such researches will give us the knowledge, so earnestly desired by metallurgists, of the nature of the physical and mechanical processes in metallic crystals, especially when combined with modern knowledge of the structure of the atom. One difficulty, however, presents itself at the outset. Ordinary masses of metal as we know them are not single crystals, but

aggregates of variously orientated small crystals, and this fact prevents us from predicting their properties from a knowledge of the space-lattice alone. Until recently we knew practically nothing of the mechanical properties of single crystals of metals, but Professor Carpenter and Miss Elam, by an ingenious device, have now been able to prepare test-pieces of aluminium consisting of a single crystal.* Such masses prove, as might be expected, to be highly plastic, and the study of their properties after extensive deformation is giving interesting results, particularly from the application of X-ray analysis. The variation of properties with orientation leads to most striking peculiarities in the behaviour of these novel test-pieces.

In normal masses of metal, the existence of intercrystalline boundaries introduces a new factor. Such boundaries are most often a source of strength, not of weakness, and there has been much speculation as to the nature of the conditions where one crystal is in contact with another in an aggregate. A suggestion made by several older authors has been adopted and greatly developed by Rosenhain, to the effect that a small residue of liquid between the grains fails to crystallise when passing through the freezing point, owing to the atoms of metal in the liquid state being attracted to two neighbouring space-lattices of different orientation, ultimately attaching themselves to neither, so that a layer without any definite orientation separates the grains in the solidified mass of metal. In spite of inherent theoretical difficulties in the way of its acceptance, this hypothesis of an "amorphous intercrystalline cement" has become popular on account of its remarkably successful application to such problems as the change of mechanical properties of metals with temperature, and the failure of metals under long-continued stress.† It should be said that for such purposes a layer at least several hundred atoms in thickness is required. Even although so thick a layer may be theoretically unacceptable, some difference of properties at the bounding surfaces must be assumed. In 1902, Quincke‡ suggested that the liquid, immediately before solidification, separates into two immiscible liquid phases, one of which forms an oily film, dividing the mass into foam cells, of which the second liquid forms the contents. On this view, the crystal grains should be geometrically similar to foam cells. In a few cases, it has been possible to test this similarity. Certain β -brasses containing aluminium disintegrate rapidly on immersion in mercury, the grains separating from one another in the course

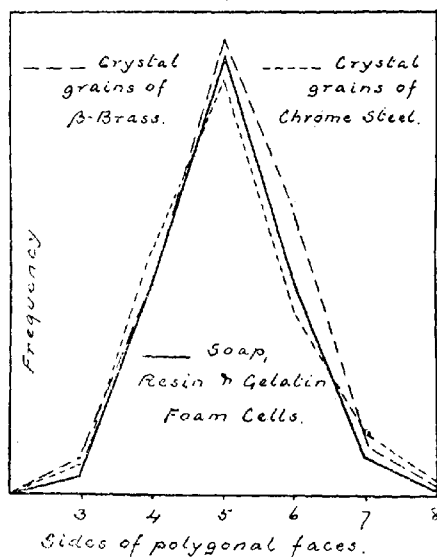
* *Proc. Roy. Soc.*, 1921, [A], **100**, 329.

† W. Rosenhain and S. L. Archbutt, *Proc. Roy. Soc.*, 1919, [A], **96**, 55.

‡ *Ann. Physik*, 1902, [iv], **9**, 1.

of a few seconds, so that they may be examined singly. Occasionally, too, a forging proves to be highly brittle, so that the crystal grains separate spontaneously. The fracture of such a forging of chromium steel is shown in Fig. 4. Such isolated grains have been compared with the cells in a foam of soap solution, resin, or gelatin, and a close similarity is found. The theoretical form of a foam cell was calculated by Lord Kelvin to be a tetrakaidecahedron having curved edges, but when any actual foam is examined, instead of four- and six-sided faces being found with frequencies in the ratio 6:8, as

FIG. 5.



required by that figure, five-sided faces are the most frequent.* In fact the individual cells tend to approximate to the pentagonal dodecahedron, slightly distorted in order that all faces may meet at an angle of 120° , as required for equilibrium between films. Space is not completely filled by such dodecahedra, and the cells are found to vary about that figure as a mean, gaps being filled by small tetrahedra and hexahedra. Observations of a large number of foam cells are collected in Fig. 5, which shows the frequency of occurrence of 3, 4, 5, 6, 7, and 8-sided faces. On the same diagram are shown corresponding observations of crystal grains from several

* *J. Inst. Metals*, 1919, 22, 241.



FIG. 4.
Crystal grains in chromium steel.

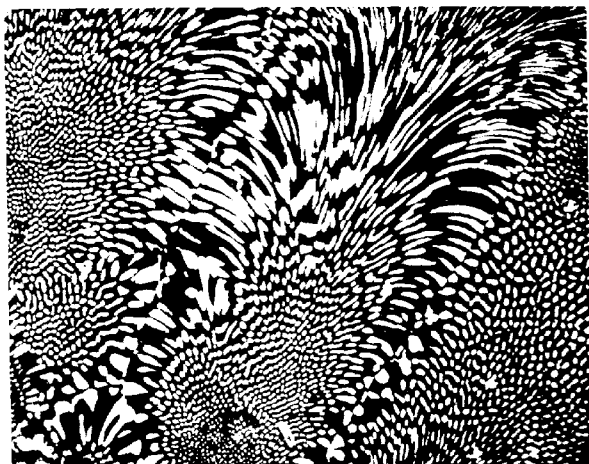


FIG. 6.
Eutectic in phosphor copper.*

* *Dr. Bragg's gift.*



FIG. 7.
Crystalline film of zinc



FIG. 8.
Surface-tension pattern on gold bead

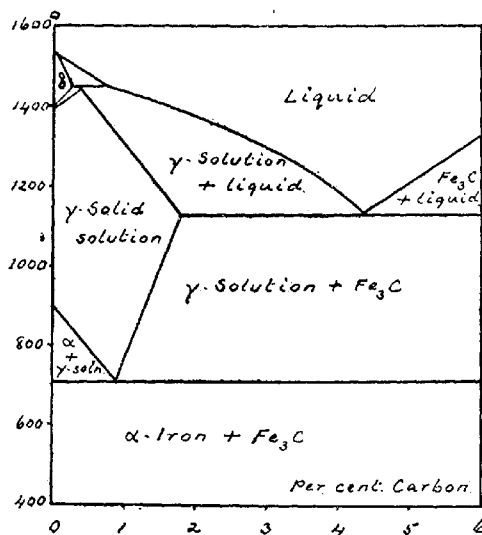
specimens of β -brass and from one of the chromium steel. It is evident that there is a very close similarity of shape between the grains and foam cells, but it does not follow that Quincke's hypothesis, which is open to objection on other grounds, is true. The evidence does, however, go far to show that the forms of the grains are determined by surface tension. During solidification, two forces are opposing one another, the directed cohesion, which causes the atoms to build themselves into a definite geometrical form, and surface tension, which tends to diminish the surface area of each growing crystal. The balance between these forces is different in different metals. Antimony, for example, readily forms sharp-edged crystals in alloys, whilst the branching growths of copper are usually rounded. In eutectic alloys, in which two metallic phases crystallise simultaneously, the effect of surface tension is often such that all angles disappear, as in the eutectic of copper and copper phosphide (Fig. 6). The crystals of zinc on the surface of a galvanised sheet are commonly sharp (Fig. 7), but a bead of gold, allowed to cool slowly from the liquid state without disturbance, has surface markings which rather suggest a purely amorphous substance, such as gelatin, than a crystalline solid (Fig. 8). When the surface layer is dissolved away by aqua regia, sharp, crystalline etch-figures appear. At a temperature far below the melting point of gold, these angular figures are again rounded under the influence of surface tension.

The study of equilibrium between metals in alloys has advanced rapidly under the guidance of the doctrine of phases, due in the first instance to Gibbs and developed by Roozeboom and others. The highly abstract conception of the thermo-dynamical potential, however, rarely applied, and the simple temperature-concentration diagram is universally used. For its construction, two methods are principally employed in conjunction, thermal analysis and microscopical observation. The latter method, applied to metals by Sorby as far back as 1864, has reached a remarkable state of perfection, and has become a routine method of examination in industrial works. Some of the metallic systems prove to be of great complexity. The copper-tin alloys, which were investigated with great care by Heycock and Neville,* whose conclusions have been in the main confirmed by later workers, are conspicuous by their complexity. Another system of great practical importance is found in the alloys of iron with carbon, a non-metallic element, forming a carbide of metallic character, Fe_3C (Fig. 9). Here the system is complicated by the allotropy of iron. The X-ray method has shown that the α -, β -, and γ -modifications of iron have identical

* *Phil. Trans.*, 1902, [A], 202, 1.

cube-centred space-lattices, varying only in dimensions with temperature, β differing only from α in being non-magnetic, whilst γ has an entirely different, face-centred cubic lattice.* The γ -modification has the property of dissolving carbon in the solid state, and on this fact depends the great variation in properties that is possible in this single system, which includes the steels. The range would be much more limited if we were restricted to stable conditions. Actually, by hastening the cooling of the alloys, they may be preserved in a metastable or labile condition,

FIG. 9.



and the industrial hardening of steel depends on this fact. Moreover, by adding other metals, such as nickel, chromium, or tungsten, it is possible to alter the position of the transformation points in the system, and very greatly to diminish the velocity of change: hence the wonderful variety of heat-treated steels at the disposal of the modern engineer. In the study of these unstable conditions, one of the most difficult branches of metallurgy, the X-ray method has again rendered valuable service. It has shown that the iron in martensite, the principal constituent of hardened steel, is in the α condition, although the method has so far failed to determine exactly the arrangement of the carbon atoms in the same steel.

* A. Westgren and G. Phragmen, *J. Iron Steel Inst.*, 1922, i, 241.

An important branch of metallurgical study is concerned with the behaviour of metals when cold-worked, that is, when deformed at temperatures removed from the melting point. Whilst great hydrostatic pressure has no permanent effect on the properties of a metal, pressure unsymmetrically applied, so as to cause plastic flow, produces changes of a far-reaching character. The hardness of the metal is increased, its density is diminished, and its store of internal energy, as shown by the heat developed when it is dissolved in a suitable reagent, is increased. Whilst Tammann and others have considered that the only change is a reduction in the size of the crystal grains, most metallurgists in this country have adopted the hypothesis of Beilby,* according to which the space-lattice of the metal is locally broken down, with the production of a vitreous or amorphous material. This assumption has been used with great success to explain the facts of cold-working. The objection has been brought against it, that it involves the production of a new phase in a region within which it is unstable, but in the light of modern views as to the nature of the space-lattice it is quite comprehensible. It has been further suggested that the amorphous material is the undercooled liquid phase, resulting from a true fusion, the melting point of the solid being lowered by non-uniform pressure, as predicted by Poynting. In confirmation of this rather startling view, it has been shown that when the pressure necessary to lower the melting point of various metals to atmospheric temperature is calculated, although the values found are very high, yet when the metals are arranged in ascending order of the pressures required, the order is that of diminishing plasticity, as measured by the flow of the metal through an orifice.†

Lowering of melting point of metals effected by one atmosphere unequal pressure; together with the computed melting pressures (in atm.) at the ordinary temperature (Johnston & Adams).

Metal.	Melting point.		Heat of fusion. Q.	Density.		Melting pressure. Atm.
	<i>t.</i>	<i>T_p.</i>		<i>D.</i>	$\Delta T_p.$	
K	62°	335°	15.7	0.87	0.59°	64
Na	97	370	31.7	0.98	0.29	266
Pb	327	600	5.4	11.37	0.24	1,760
Sn	232	505	14.1	7.29	0.12	2,200
Bi	270	543	12.5	9.80	0.11	3,600
Cd	321	594	13.7	8.64	0.12	3,500
Al	658	931	42.0	2.60	0.21	5,100
Zn	419	692	28.0	7.1	0.084	6,900
Ag	960	1,233	23.0	10.50	0.12	14,000
Cu	1,083	1,356	43.0	8.93	0.086	24,000
Pd	1,550	1,823	36.3	11.4	0.11	31,000
Ir	1,755	2,028	27.2	21.5	0.084	46,000

* *Phil. Mag.*, 1904, [vi], 8, 258.

† *J. Johnston, J. Amer. Chem. Soc.*, 1912, 34, 788.

Examination by the X-ray method is naturally unable to detect whether small quantities of amorphous material are formed, but it has shown that, at least in certain metals, especially tungsten, extensive cold-drawing leads to a rearrangement of the elongated crystal grains, the orientation of the majority of the grains becoming similar, so that the wire has a fibrous structure.* Much is to be expected from this line of research, which supplements the older and still indispensable method of microscopical examination.

Only a few topics have been selected from the very numerous metallurgical applications of physical chemistry, but they will serve to indicate the large field for co-operation between the physical chemist and the metallurgist. The subjects that have been mentioned are by no means of academic interest only. The successful conduct of the metallurgical industries depends on their scientific handling. A modern steel works, concerned with the manufacture of the higher classes of engineering steels, must be equipped for the making of thermal, microscopical, magnetic, and dilatometric determinations, and that not only for research purposes, but in the regular control of works processes. New discoveries in this branch of science have not to wait long for their practical application.

XXXVI.—*The Constitution of the Disaccharides.* *Part VII. Sucrose.*

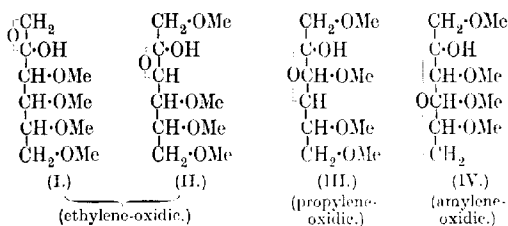
By WALTER NORMAN HAWORTH and WILFRED HERBERT LINNELL.

THE constitutional formula for sucrose which was proposed in Parts I and IV of this series of communications (T., 1916, 109, 1314; 1920, 117, 199) represented the γ -fructose residue in the biose as containing an ethylene-oxidic structure. This view was expressed at an early stage of our work, and after an endeavour to solve this problem by oxidising the tetramethyl fructose obtained on hydrolysing octamethyl or heptamethyl sucrose. The conditions under which this oxidation was conducted were similar to those usually followed by Fischer and Kiliani in the sugar series. Tetramethyl γ -fructose yielded, on digestion with dilute nitric acid at 60°, a viscid liquid which distilled with difficulty and corresponded with an anhydro-acid or semi-lactide, $C_{10}H_{12}O_5(OMe)_6$.

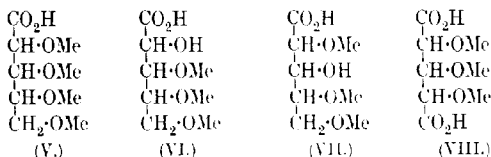
In offering an interpretation of this result it was stated that "although the additional evidence here contributed appears capable of no simple explanation other than that now offered.

* M. Ettisch, M. Polanyi, and K. Weissenburg, *Z. physikal. Chem.*, 1921, 90, 332.

the constitution of the new form of tetramethyl fructose is being further investigated in view of the importance of the issues." The present work is therefore an extension of the earlier inquiry and, as before, attention is focussed on the nature of the internal linking of the oxide ring in the fructose fragment. The cyclic structure in the latter differs from that of ordinary butylene-oxidic fructose, and the choice of a constitution for the tetramethyl γ -fructose derived from methylated sucrose appears to be limited to one of the following :



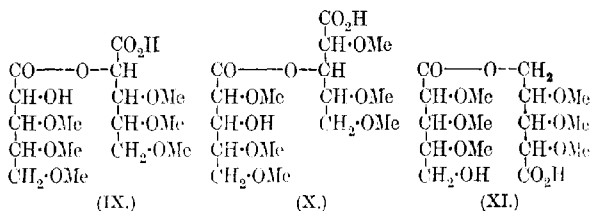
Reviewing the evidence of oxidation, it appeared that a tetramethyl γ -fructose represented by formula IV should give rise to a dibasic acid (trimethoxyglutaric acid) on oxidation with nitric acid, the reducing group associated with the second carbon atom yielding one carboxyl group, and the potential primary alcohol residue in the terminal position yielding a second carboxyl group corresponding with the sixth carbon atom of the hexose chain. The expected product may be formulated as below (VIII) :



On the other hand, a fructose derivative formulated as in II or III should give rise to an α - or β -hydroxy-acid (VI or VII) which has its terminal primary alcoholic group, at the sixth carbon position, protected by methoxyl; whilst the product (V) expected from a sugar of the constitution shown in formula I differs from the other three inasmuch as four methoxyl residues are retained.

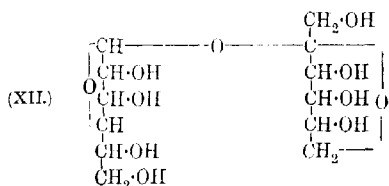
In the earlier research the product of oxidation did not correspond with any of these simple formulæ. The compound isolated, $\text{C}_{10}\text{H}_{12}\text{O}_5(\text{OMe})_6$, had a molecular complexity almost twice as great as was anticipated, and this agreed with the theoretical

values for a semi-lactide. Although three possible structural formulæ for such a compound are shown below, yet the simple explanation was that this behaviour closely resembled that of an α -hydroxy-acid, such as lactic acid. On the whole, the evidence favoured the view that an acid of the formula VI could most reasonably give rise to a semi-lactide such as is shown in formula IX.



The second of these formulæ was rejected on the ground that the simple β -hydroxy-acid (VII) from which the semi-lactide (X) might be derived would preferably form a β -lactone, whilst formula XI was similarly deemed improbable, since a δ -hydroxy-acid would be expected to form a δ -lactone, and moreover the appearance of a δ -hydroxy-acid, which contained a free primary alcohol residue, as an oxidation product was regarded as anomalous under the experimental conditions employed. It seemed more probable that such a hydroxy-acid would pass at once into the dibasic acid (VIII).

Extension of this research during the past two years has led to a revision of these views and appears to us to have established beyond reasonable doubt that the structure of tetramethyl γ -fructose is no longer to be regarded as ethylene-oxidic but amylenic-oxidic in character. Consequently the constitution ascribed earlier to sucrose must be modified and replaced by the new formula XII:



This conclusion has been reached by again submitting tetramethyl γ -fructose to oxidation with dilute nitric acid under modified conditions, the chief variation from the earlier experiments being a more prolonged digestion with this reagent.

The chief product was a lactone of a monobasic acid distilling

readily at 129°/0.1 mm., showing n_D 1.4565 and $[\alpha]_D + 18.5^\circ$, which value changed in sixteen hours to $+ 36.0^\circ$. This agreed in properties and analytical data with the requirements of a trimethoxyvalerolactone, $\text{CO}[\text{CH} \cdot \text{OMe}]_3 \cdot \text{CH}_2$.

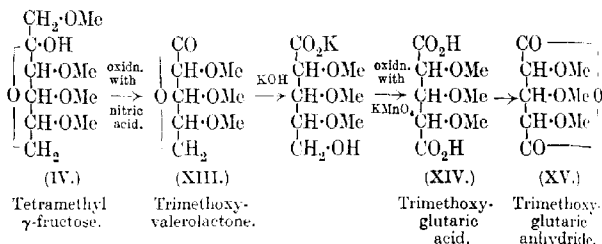
Accompanying this product was a small quantity of a substance distilling with decomposition at 190°/0.08 mm. The latter appeared to be identical with the semi-lactide obtained in the earlier experiments, but the following argument demonstrates that this must now be formulated as shown in XI.

Investigation of the trimethoxyvalerolactone showed that, after exposure to moist air, a portion underwent transformation into a crystalline substance, for which the provisional melting point is given as 83°, and this may be either the polymeride of the lactone or the free hydroxy-acid. The behaviour of the lactone differed from that expected of a β - or γ -lactone, although the evidence available at this stage left the decision indefinite whether the lactone had been formed from a β -, γ -, or δ -hydroxy-acid. If it could be shown that the trimethoxyvalerolactone was capable of transformation into trimethoxyglutaric acid by oxidation, a solution of the outstanding difficulty was clear, since this would afford conclusive evidence that the lactone contained a potential primary alcohol group as a terminal group in the chain of five carbon atoms. Accordingly, the lactone was dissolved in aqueous potassium hydroxide in order to open the lactone ring, and the corresponding salt of trimethyl tetrahydroxyvaleric acid was oxidised with alkaline permanganate. In the first instance the utilisation of the permanganate was measured by titration, and it was observed that each molecular proportion of trimethoxyvalerolactone required one molecular proportion of oxygen. The reaction proceeded instantaneously at 70°, but at the ordinary temperature the period required was about eight hours.

The main or only product of this oxidation was a colourless liquid, distilling at 100°/0.05 mm. with separation of some moisture in the first stage of the distillation. It had all the characteristics of an anhydride of a dibasic acid, $\text{C}_5\text{H}_{14}\text{O}_7$, and analytical data showed that the substance was trimethoxyglutaric anhydride, from which a specimen of the dimethyl ester of trimethoxyglutaric acid (XIV) was prepared. The only formula available for the primary oxidation product from which these latter compounds were derived is that of the δ -lactone (XIII). On this evidence it is permissible to ascribe a definite formula, IV, to tetramethyl γ -fructose, provided that one excludes such an exceptional possibility as the elimination of a terminal methyl group from an acid of the formula

V in the course of the oxidation of a substance of the constitution represented by I. The latter consideration will be dealt with in the succeeding communication.

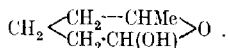
It may be stated, however, that in the exceptional case quoted by Irvine and Hirst (T., 1922, **121**, 1312) the removal of a methoxyl residue during oxidation with nitric acid was the accompaniment of oxidation of the exposed group to carboxyl. The circumstances in the present case differ in that no oxidation of the terminal alcohol group occurs. Indeed it would appear that under the influence of nitric acid the amylene-oxide ring in the original sugar remains undisturbed, passing to the analogous δ -lactone structure, which is then resistant towards oxidation at the point where a potential primary alcohol group exists.



Unexpected as this result may seem, and far-reaching as are its implications, it is to be welcomed for the reason that it serves to clarify many existing anomalies in the literature of the γ -sugars. Possibly it is premature to ascribe the amylene-oxide structure to the γ -sugars in general, but it is permissible to review certain data which are not opposed to this view. Tetramethyl γ -glucose gave on oxidation with permanganate a tetramethyl gluconolactone (Irvine, Fyfe, and Hogg, T., 1915, **107**, 509) which differed from the ordinary tetramethyl gluconolactone first obtained by Purdie and Irvine (T., 1903, **83**, 1033). Cunningham observed that maltose gave rise to a γ -methyl maltoside in presence of hydrogen chloride dissolved in methyl alcohol, but failed to form the analogous compound from lactose (T., 1918, **113**, 695). The explanation of this non-success may lie in the fact that the structure of lactose, as has been shown by Haworth and Leitch, precludes the formation of an amylene-oxide ring inasmuch as the group attached to the fifth carbon atom of the glucose chain is involved already in the linking of the two hexoses.

Furthermore, there appears on record no example of internal oxide ring formation in the case of glycollic or glyceric aldehydes,

whilst Helferich and Malkomes (*Ber.*, 1922, **55**, [B], 702) have shown that 8-hydroxyhexaldehyde exists as the cyclic or amyleno-oxidic form :



This compound displays very tardily in solution certain aldehydic properties, due to the opening of the ring.

The ease of hydrolysis of sucrose or γ -glucosides is explicable on the assumption that the amyleno-oxide ring opens by the agency of acids of extreme dilution, thus disturbing the disaccharide or glucosidic linking, which then undergoes hydrolytic cleavage. In the case of sucrose, the fructose fragment then passes, by structural changes, to the butylene-oxide form, which is more stable in aqueous solution.

EXPERIMENTAL.

Oxidation of Tetramethyl γ -Fructose with Nitric Acid: Isolation of a Lactone, $\text{C}_8\text{H}_{14}\text{O}_5$.

Tetramethyl γ -fructose was prepared by the hydrolysis of heptamethyl sucrose, following the conditions previously determined (Haworth, T., 1915, **107**, 9; 1920, **117**, 119). In the latter communication, the oxidation of this product was described, tetramethyl γ -fructose being subjected to treatment with dilute nitric acid (*d* 1.2) at 60° for six hours, which is the usual period allotted to similar reactions in the sugar group. In the present instance, the oxidation was conducted for a prolonged period at 60° , and in all cases the reaction terminated after twenty hours. Extraction and isolation of the product were effected by the usual methods.

This oxidation, which has been carried out with many specimens of tetramethyl γ -fructose, was found to give rise in every case, under the prescribed conditions, to a pale yellow liquid (fraction A) which distilled at $129^\circ/0.1$ mm. and showed n_D^{20} 1.4565 and $[\alpha]_D^{20} + 18.5^\circ$ in water, changing in sixteen hours to $+ 36.0^\circ$. The residue was dark in colour and this distilled with decomposition at $190^\circ/0.08$ mm. (fraction B) as a viscid syrup.

Fraction A on analysis gave the following data :

Found : C = 50.5; H = 7.26; OMe = 47.3. $\text{C}_8\text{H}_{14}\text{O}_5$ requires C = 50.53; H = 7.37; OMe = 48.9 per cent. On titration with dilute alkali the liquid showed the usual behaviour of a lactone, combination with alkali being extremely slow in the cold.

0.1857 Gram required 9.85 c.c. of $N/10\text{-NaOH}$ for complete neutralisation after digestion under reflux for twenty minutes, whereas a lactone, $\text{C}_8\text{H}_{14}\text{O}_5$, should require 9.77 c.c. All the analytical data have been several times confirmed. A molecular

weight determination by the cryoscopic method, using a benzene solution, gave the value 211; the theoretical value being 190.

On keeping the liquid, representing fraction A, in a loosely corked tube, a portion crystallised. The crystals were washed with light petroleum and then melted at 83° with previous softening at 79° ; the quantity collected, however, was small and the compound was not recrystallised, so that the melting point of the substance is given with reservation. When dissolved in water, the crystals showed an acid reaction, decolorised permanganate, and did not reduce Fehling's solution. On titration, the substance behaved throughout as an acid and not as a lactone, neutralisation being complete without the application of heat.

0.0818 Gram required 38.3 c.c. of $N/100\text{-NaOH}$, whilst an acid, $\text{C}_8\text{H}_{16}\text{O}_6$, requires 38.53 c.c.

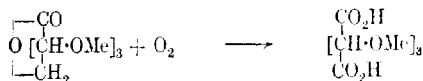
Found: $\text{OMe} = 41.5$. $\text{C}_8\text{H}_{16}\text{O}_6$ requires $\text{OMe} = 44.7$ per cent.

*Oxidation of the Lactone $\text{C}_8\text{H}_{14}\text{O}_5$ with Alkaline Permanganate.
Formation of Trimethoxyglutaric Acid.*

Preliminary experiments were instituted with the view of devising conditions for the oxidation of the lactone, representing fraction A, by the agency of alkaline permanganate. An aqueous solution containing 1 per cent. of the lactone was used; to 10 c.c. of this solution, N -sodium hydroxide solution (2 c.c.) was added and this mixture titrated with $N/10$ -potassium permanganate, the whole being maintained at 70° during the operation. After each addition of the permanganate an interval was allowed for the manganese oxides to separate and the solution to clear, and this was continued until a permanent pink coloration appeared, a trace of hydrogen peroxide serving to destroy the slight excess of permanganate. The following were the results of two experiments:

1. 10 c.c. of lactone solution required 35.0 c.c. of $N/10\text{-KMnO}_4$.
2. 10 c.c. of lactone solution required 35.5 c.c. of $N/10\text{-KMnO}_4$.

From the calculation it appeared that four molecular proportions of alkaline permanganate were required for the oxidation of three molecular proportions of the lactone $\text{C}_8\text{H}_{14}\text{O}_5$, and the reaction may be expressed by the equation:



Having established these conditions, several experiments were conducted with larger quantities in order to isolate the product. Since the organic dibasic acid which might be anticipated was, however, in the form of a salt, the isolation was facilitated by using

potassium hydroxide as the alkali, in order that the free organic acid could be liberated by the addition of the exact proportion of perchloric acid. Removal of the potassium perchlorate by means of alcohol and ether was then a simple procedure.

Consequently 2.5 grams of the lactone $C_8H_{14}O_5$ were dissolved in 500 c.c. of water, to which were added 25 c.c. of 2*N*-potassium hydroxide and then, gradually, the calculated quantity of permanganate at 70°. After passing carbon dioxide through the cold solution and separating the manganese oxides, much of the water was removed by distillation under diminished pressure. Adding to the residual solution the calculated amount of perchloric acid along with alcohol for the precipitation of the potassium, the filtrate now consisted of an aqueous alcoholic solution of the organic dibasic acid. This product was then isolated and distilled, when a straw-yellow, slightly viscid liquid was collected at 100°/0.05 mm. (Found: C = 47.0; H = 6.18; OMe = 44.3. $C_8H_{14}O_7$ requires C = 43.6; H = 6.4; OMe = 45.4 per cent. $C_8H_{12}O_6$ requires C = 47.1; H = 5.9; OMe = 45.1 per cent.). On titration with *N*/10-NaOH, 0.047 gram combined with 4 c.c. of the alkali without heating. In all, 10.1 c.c. of the alkali were added and the solution was heated at 90° for twenty minutes. Thereafter, 5.55 c.c. of *N*/10-HCl were required for neutralisation. The compound had therefore combined with 4.55 c.c. of *N*/10-NaOH, whereas a substance $C_8H_{12}O_6$ should require 4.60 c.c. Several specimens from different preparations gave identical analytical results.

The compound isolated appeared therefore to have the constitution of a trimethoxyglutaric anhydride, $C_8H_{12}O_6$.

Digestion with 2 per cent. methyl alcoholic hydrogen chloride for six hours gave rise to the corresponding dimethyl ester. This distilled at 89–92°/0.07 mm. and showed n_D^{20} 1.4419 and $[\alpha]_D^{20} + 48.7^\circ$ in water ($c = 0.72$) (Found: C = 48.38; H = 7.23; OMe = 59.7. $C_{10}H_{18}O_7$ requires C = 48.0; H = 7.2; OMe = 62.0 per cent.).

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[Received, December 6th, 1922.]

XXXVII.—*The Constitution of the Disaccharides. Part VIII. Sucrose.*

By WALTER NORMAN HAWORTH and JAMES GIBB MITCHELL.

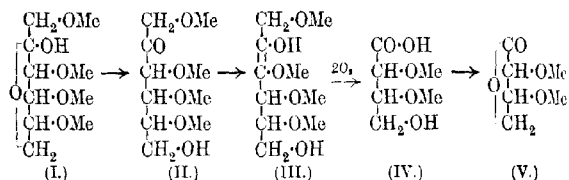
THE preceding paper on the constitution of sucrose contributes evidence derived from the oxidation of tetramethyl γ -fructose with nitric acid. The interpretation therein outlined receives support

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and confirmation from the series of experiments which are now to be described. Tetramethyl γ -fructose, obtained as a cleavage product of octamethyl or heptamethyl sucrose, has been oxidised with alkaline permanganate, and the chief product isolated is shown to be dimethoxybutyrolactone (V).

The circumstance that degradation of the methylated fructose residue leads to the isolation of a product containing a chain of four carbon atoms illustrates very strikingly that with an alkaline oxidising agent the hexose is attacked in a totally different manner from what has been shown to be the case with an acid oxidising agent. Whereas with nitric acid degradation occurs by fission of the hexose chain between the first and second carbon atoms, giving rise to a derivative of δ -valerolactone, on the other hand alkaline permanganate would appear to promote ketonisation and enolisation with the introduction of a double linking between the second and third carbon atoms, following which rupture occurs at the ethylenic bond

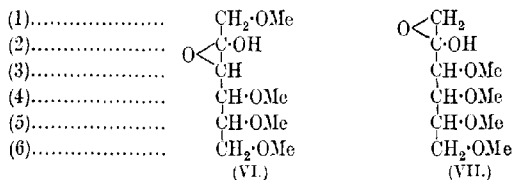


Attention has been focussed on the quantitative aspect of this oxidation. It was shown that during the transformations expressed in the preceding formulæ four atomic proportions of oxygen were utilised for each molecular proportion of sugar.

Dimethoxybutyrolactone was isolated both in this form and as the potassium salt of the open-chain acid, dimethyl trihydroxybutyric acid (IV). In the latter form it must originally have appeared during the course of the oxidation with alkaline permanganate. Significance is attached to the fact that before acidifying the product consisting of the above potassium salt a methyl group was absent from the terminal position in the chain. Evidence is not lacking for the supposition that lactonisation of an acid of this character may occur by elimination of a methyl group from one of the positions occupied by methoxyl where lactone formation may be expected (Denham and Woodhouse, T., 1917, 111, 244). This contingency did not appear to arise in the present case, since it was clearly shown that the salt of the substituted butyric acid which was isolated contained, in common with the lactone, two methoxyl residues only.

Certain observations indicated that the oxidation of tetramethyl γ -fructose with alkaline permanganate proceeded in two stages. When the quantity of permanganate corresponded with the introduction of two atomic proportions of oxygen, this seemed to satisfy for some time the full requirements; but on keeping this alkaline solution for several hours it developed the capacity to absorb more oxygen, equal in amount to the first. This circumstance is explicable on the assumption that the methyl ester of dimethyl trihydroxybutyric acid is the first product of oxidation, the alkali present afterwards liberating methyl alcohol by hydrolysis, which then undergoes oxidation to formic acid. Regulated oxidation of this kind may prove to be the key to many of the difficult problems involved in sugar degradations.

The bearing of these results on the constitution of sucrose is made clear by the following considerations. As reference to the earlier papers in this series will show, the glucose residue in sucrose is definitely of the butylene-oxidic type. The fructose residue, however, is present as a γ -sugar, and it was formerly suggested as the result of a study of tetramethyl γ -fructose that the structure of this compound was best represented by the formula VI, although other possible formulæ were kept in view.



There can no longer remain any doubt that this formula must be revised, since it is now established that the carbon atom 3, indicated above, cannot be concerned in the internal oxide linking, inasmuch as this carbon atom must be associated with a methoxyl group in order that the sugar may give rise to trimethoxyglutaric acid, one of the products of degradation described in the preceding paper (Haworth and Linnell).

An alternative ethylene-oxide structure (VII) might meet the case provided it were allowable, during the course of the oxidation with the selected reagents, for the methoxyl group attached to the sixth carbon atom to suffer expulsion, with the consequent introduction of carboxyl at both the second and sixth positions in the chain. But trimethoxyglutaric acid was only formed as the result of further oxidation of the primary oxidation product which was isolated, namely, the δ -valerolactone, and it appears unreasonable

to suppose that, if lactone formation occurred by elimination of a methoxyl residue from a position in the hexose chain, the residue expelled should be that attached to carbon atom 6 rather than 5, since the latter choice would lead to the more usual γ -lactone.

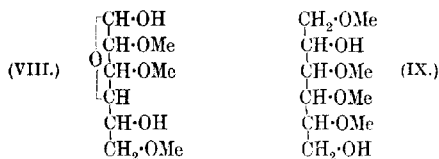
Severance of the hexose chain between the second and third carbon atoms by the agency of alkaline permanganate gave rise, however, to dimethoxy- γ -butyrolactone, whereas if the fructose fragment were to be formulated as in VI, then the product normally to be expected would be trimethoxybutyric acid. That the terminal methoxyl group in a compound such as the latter is not prone to removal by lactone formation was shown by Irvine and Hynd (T., 1909, 95, 1226), who obtained $\alpha\beta$ -dihydroxy- γ -methoxybutyric acid by oxidation of 6-methyl fructose (butylene-oxidic). Moreover, it would indeed be remarkable to encounter the loss of a methoxyl group in alkaline solution without the concomitant of oxidation of the terminal $-\text{CH}_2\text{OMe}$ group to $-\text{COOMe}$, and it is clearly shown that before isolation of the dimethoxy- γ -butyrolactone by means of mineral acid, the primary oxidation product was potassium γ -hydroxy- $\alpha\beta$ -dimethoxybutyrate.

Acceptance of both formulæ VI and VII seems therefore to be precluded by the evidence of oxidation, and these ethylene-oxidic formulæ must therefore be abandoned. A propylene oxide structure is also inconsistent with the facts, and the only constitution which fully meets the case for tetramethyl γ -fructose is that which represents this compound as containing an amylene-oxide ring as shown in formula I. It follows that the allocation of a structural formula to sucrose is simplified, and this now consists in butylene-oxidic glucose linked with amylene-oxidic fructose by union of these hexoses through their reducing groups.

Other data bearing on the constitution of heptamethyl sucrose may now be furnished. It was previously demonstrated that in this compound the glucose residue was partly substituted by methyl groups and a liquid trimethyl glucose was isolated (Haworth, *loc. cit.*). It is shown that this sugar, which has now been obtained in the crystalline form, must be represented by formula VIII.

Octamethyl sucrose has been prepared by a new method which dispenses with the use of methyl iodide. Also it was found in the course of this work that a γ -sugar may be easily separated from a sugar of the butylene-oxidic type by taking advantage of the ease with which glucoside formation may be promoted in the cold with sugars of the former class. This is paralleled in other groups of compounds by several examples of unsaturated acids in which separation may be effected by preferential esterification or hydrolysis (compare Haworth and Perkin, T., 1908, 93, 585).

The reduction of tetramethyl γ -fructose with sodium amalgam and moist ether gave rise to a compound having all the properties of a tetramethyl hexitol, and consisting probably of both the mannitol and sorbitol derivatives. These showed a specific rotation of $+10.8^\circ$ in water, and this value was not influenced by the introduction of boric acid. Böcseken's results tend to show that where no exaltation of specific rotation occurs by the addition of boric acid, the compound ordinarily does not contain two hydroxyl groups attached to contiguous carbon atoms. It will be seen that the structure (IX), allocated to the tetramethyl hexitols on the basis of the previous discussion, fulfils this condition.



EXPERIMENTAL.

Oxidation of Tetramethyl γ -Fructose with Permanganate.

Preliminary experiments were instituted in order to determine the volume of a standard permanganate solution necessary for the oxidation of tetramethyl γ -fructose. Using neutral permanganate in the cold, the whole of the sugar did not undergo oxidation. The instantaneous decoloration of permanganate by the γ -sugar, which has been regarded as a characteristic reaction of sugars of this class, ceased after the addition of a few drops of very dilute permanganate, and thereafter the decoloration was extremely slow. The reaction appeared to be complete, however, long before one atomic proportion of oxygen had been supplied. On the other hand, when alkali was added, the instantaneous oxidation of the sugar proceeded provided the alkalinity was maintained.

An explanation of this behaviour is that a small proportion of the γ -sugar is originally present in an enolic form, and that it is this form which normally is responsible for the characteristic permanganate test for these compounds. Enolisation may, however, be induced by the addition of alkali, and so long as alkali is present the whole of the sugar can combine with oxygen and undergo scission at the double linking which is introduced as the result of enolisation. The sensitiveness of tetramethyl γ -fructose towards alkali is illustrated by the fact that the specific rotation is diminished in presence of very dilute sodium hydroxide from $+31^\circ$ to -19° in the course of a few hours.

Acid oxidising agents, on the other hand, attack this γ -sugar less speedily than alkaline permanganate, and it is remarkable that oxidation proceeds scarcely at all with bromine water. It may be remarked that some discrepancy appears to have entered into the literature of the γ -sugars concerning the use of the permanganate test. Almost all sugars, whether butylene-oxidic or those of the γ -type, respond quickly towards alkaline permanganate, but the butylene-oxidic forms decolorise neutral permanganate only tardily, and it is this latter reagent which is normally applied for the detection of a γ -sugar.

Isolation of Dimethoxybutyrolactone.

Trial oxidation experiments were conducted with the aid of a solution containing 1.78 grams of tetramethyl γ -fructose in 200 c.c. of water. Five c.c. of this solution, to which 1 c.c. of *N*-sodium hydroxide was added, required 28.4 c.c. of 0.092*N*-permanganate. The results pointed to the utilisation of four atomic proportions of oxygen for each gram-molecule of the sugar. From the initial titration experiments there remained over exactly 185 c.c. of the sugar solution, containing 1.167 grams of tetramethyl γ -fructose. To this was added 12 c.c. of 2*N*-sodium hydroxide and such a volume of the permanganate solution as corresponded with four atomic proportions of oxygen. On keeping for several days at room temperature, the solution showed a faint green colour and this was discharged by the addition of a trace of hydrogen peroxide or alcohol. After passing through the solution a stream of carbon dioxide to eliminate the free alkali and finally filtering from the precipitate of manganese oxides, the clear solution was evaporated in a vacuum and yielded a yellow solid.

Extraction of this solid, first with ether and then with chloroform, removed a small quantity of syrup. The residue was dissolved in acidified water and extracted with ether in the Hageman apparatus. On drying the extract and evaporation of the solvent, a syrupy residue was obtained which showed a faintly acid reaction. Distillation of a trial portion of this product yielded a colourless liquid boiling at 130–135°/0.14 mm. with considerable darkening of the residue. This gave $\text{OMe} = 41.4$ per cent., showed $n_D^{20} 1.4419$, and the product was titrated with alkali:

0.1165 Gram required 8.16 c.c. of *N*/10-NaOH for complete neutralisation after heating, and behaved throughout as a lactone. A lactone, $\text{C}_6\text{H}_8\text{O}_2(\text{OMe})_2$, of a monobasic acid should require 8.0 c.c. A determination of molecular weight in benzene solution by the cryoscopic method gave the values 159 and 165, whereas the above formula requires 146. Since a very small proportion

of this distilled product had crystallised on keeping, it is possible that the compound shows a tendency to polymerise.

The major portion of the compound was prepared for analysis without submitting it to distillation, and this was dried at 80° in a high vacuum:

0.1730 Gram required 11.64 c.c. of *N*/10-barium hydroxide for neutralisation after heating at 90°, whilst a compound of the above formula requires 11.84 c.c.

Found: C = 48.96; H = 6.38; OMe = 40.5. $C_4H_4O_2(OMe)_2$ requires C = 49.3; H = 6.84; OMe = 42.4 per cent. For the purpose of purification, the barium salt was prepared (Found: C = 30.96; H = 4.92; Ba = 29.74. Calc., C = 31.07; H = 4.75; Ba = 29.65 per cent.).

An attempt was made to conduct the oxidation with barium permanganate in presence of barium hydroxide, but the former reagent which was supplied to us was found to be chiefly the potassium salt. Ultimately 4.07 grams of tetramethyl γ -fructose were submitted to oxidation in alkaline solution, the permanganate being added gradually in the cold until the colour was no longer discharged by more of the reagent. Thereafter the isolation of the product followed the usual procedure and, on evaporation of the neutralised and filtered solution, a syrup was recovered containing the potassium salt of an organic acid along with traces of mineral salts. Treatment with alcohol removed the latter, and this was followed by extraction with ether, in which the main product was insoluble. The ether contained a substance which reduced Fehling's solution readily, whilst the insoluble residue was devoid of this property, and weighed 4 grams. This latter compound was dried and submitted to analysis; it appeared to be the potassium salt of dimethyl trihydroxybutyric acid, $OH \cdot CH_2 \cdot [CH \cdot OMe]_2 \cdot CO_2K$ [Found: K = 19.30; OMe = 29.5. $C_3H_5O(OMe)_2 \cdot CO_2K$ requires K = 19.31; OMe = 30.7 per cent.].

Attempted Oxidation of Tetramethyl γ -Fructose with Bromine.

Bromine (10.4 grams) in 40 c.c. of water was gradually added to an aqueous solution of 4.8 grams of tetramethyl γ -fructose, the mixture being surrounded with cooled water and agitated for twelve hours. Thereafter the unchanged bromine was removed under diminished pressure at 40°, more water being added from time to time as the bulk diminished. Finally, the solution was concentrated in a vacuum, neutralised with silver carbonate, filtered, and the dissolved silver eliminated as sulphide. Evaporation, followed by drying in a vacuum, led to a mobile liquid

distilling at 95—97°/0.01 mm. The analysis and physical properties indicated that this compound was unchanged tetramethyl γ -fructose.

Condensation of Tetramethyl γ -Fructose with Methyl Alcohol.

A specimen of tetramethyl γ -fructose was dissolved in methyl alcohol containing 0.25 per cent. of hydrogen chloride, the concentration of the sugar present being 2.4 per cent. This was maintained at room temperature and polarimetric readings were taken.

Time in minutes.	$[\alpha]_D^{15}$.	Time in minutes.	$[\alpha]_D^{17}$.
6	+19.9°	184	+36.4°
28	22.0	236	38.3
45	23.0	271	40.3
70	25.9	1,400	49.8
95	28.8	7,200	57.7
143	33.0		

When the solution was heated to 35°, a temporary fall in rotation was observed, but the original value was restored on cooling to room temperature. After 1700 minutes, the solution was devoid of action towards Fehling's solution. At this period, therefore, the condensation was complete, and the subsequent increase in rotation up to +57.7° could only have been due to a change in the proportions of α - and β -forms present on keeping in the solvent. As will be shown later, the specific rotation of the distilled fructoside was +48.8° in water, and it is probable that the stereochemical forms are interconvertible by heating or cooling.

When the above solution was heated to 35°, a temporary fall in rotation was observed, but the former value was restored as soon as the solution cooled to room temperature. It is interesting to correlate this phenomenon with the similar observation of Purdie and Paul (T., 1907, **91**, 296), whose records show a diminution of laevorotation when fructose undergoes condensation with methyl alcohol. In this case, the optical value tends to approach towards dextrorotation if the solution is heated above room temperature during the condensation, but here again the variation is only temporary.

The above methyl alcoholic solution was neutralised with barium carbonate, the mineral salts were removed, and the product was isolated by the recognised procedure, when an amber-coloured syrup was obtained which had no action on Fehling's solution and distilled as a colourless liquid at 137—139°/13 mm. and showed n_D 1.4461. It decolorised neutral permanganate instantly (Found: C = 52.8; H = 8.82; OMe = 59.9 per cent.).

Irvine and Steele and, later, Menzies (T., 1920, **117**, 1487; 1922, **121**, 2246), describe the preparation of this compound, namely

tetramethyl γ -methylfructoside, by a different method and from material derived from another source. It is interesting to compare the polarimetric data of this substance with those previously recorded :

Solvent.	c.	$[\alpha]_D^{25}$.
Water	2.42	+ 48.8°
Ethyl alcohol	2.95	38.7
Methyl alcohol	2.32	40.0

Isolation of Tetramethyl γ -Fructose from Octamethyl Sucrose.

Two advances have been made on the methods described in the earlier work. It is now shown to be possible to methylate sucrose completely with methyl sulphate, and also to separate by an entirely new procedure the γ -fructose from the glucose fragment.

Whilst under the usual conditions of experiment heptamethyl sucrose was the ultimate product obtained by methylating sucrose with methyl sulphate (Haworth, *loc. cit.*), yet by varying these conditions, namely, by conducting the second and third methylations in much more dilute solutions and using a larger excess of methyl sulphate and sodium hydroxide, it was found that almost the whole of the product was octamethyl sucrose, distilling constantly at 176°/0.3 mm. and having n_D 1.4582. The use of methyl iodide for the introduction of the eighth methyl group was therefore no longer necessary.

Hydrolysis with 0.4 per cent. hydrochloric acid led to a mixture of tetramethyl glucose (butylene-oxidic) and tetramethyl γ -fructose. These two products cannot be separated by fractional distillation owing to the similarity of their boiling points. Taking advantage of the fact that the fructose fragment condenses with methyl alcohol at room temperature, whilst the glucose residue requires prolonged digestion at a higher temperature to effect condensation with this reagent, a process of separation was readily devised. The mixture of compounds obtained on hydrolysis of octamethyl sucrose was dissolved in methyl alcohol containing 0.12 per cent. of hydrogen chloride, and the solution was kept at room temperature for four days. The specific rotation increased gradually to a constant value, and finally the products were worked up in the usual way and distilled, when tetramethyl γ -methylfructoside boiling at 137—139°/13 mm. was collected, whilst the tetramethyl glucose, having now a considerably higher boiling point, was left in the distilling flask, and crystallised.

Reduction of Tetramethyl γ -Fructose.

Tetramethyl γ -fructose (4.5 grams), dissolved in 50 c.c. of moist ether, was stirred under reflux in a well-cooled vessel, and carbon

dioxide was passed through the solution. During twenty-three hours, 293 grams of 2.5 per cent. sodium amalgam were added, and the volume of liquid was kept constant by adding more ether from time to time. Following the filtration of the sodium bicarbonate, the ethereal solution and washings were dried and the solvent distilled, when a colourless syrup remained. A portion of this distilled at 171°/17 mm. and showed n_D 1.4572; the remainder was prepared for analysis by careful drying in a vacuum (Found: C = 50.79; H = 9.06; OMe = 51.2. $C_{10}H_{22}O_6$ requires C = 50.42; H = 9.25; OMe = 52.1 per cent.). This result corresponded with a tetramethyl hexitol, and the product evidently was a mixture of both tetramethyl mannitol and sorbitol. It showed $[\alpha]_D^{25} + 10.8^\circ$ in aqueous solution ($c = 2.5$). The addition of 0.1 gram of boric acid to 10 c.c. of the solution produced no change in the specific rotation.

Isolation of Crystalline Trimethyl Glucose from Heptamethyl Sucrose.

In the hydrolytic cleavage of heptamethyl sucrose by dilute acid, the glucose fragment was represented by a trimethyl glucose (Haworth, *loc. cit.*). This was readily separated from the accompanying tetramethyl γ -fructose, since its boiling point was considerably higher than that of the latter compound. On repeating this work with the view of allocating a structural formula to this trimethyl glucose, the compound distilled at 165–170°/0.4 mm. and showed n_D 1.4795 (Found: OMe = 41.4 per cent.).

The substance partly crystallised on keeping, and the semi-crystalline syrup was dissolved in dry ether, treated with charcoal, and the solution concentrated. Large, acicular crystals were soon deposited, which melted at 124°. Polarimetric records showed mutarotation during one day from $[\alpha]_D + 118.4^\circ$ to $+ 69.3^\circ$. When this substance was mixed with a purified specimen of the crystalline trimethyl glucose obtained by Haworth and Leitch in the course of their work on lactose, the melting point showed no depression, thus confirming the identity of the two specimens. The structure is therefore to be represented by the formula VIII.

The authors are grateful to the Carnegie Trust for a scholarship which enabled one of them to engage in this work. They also express their thanks to Mr. W. H. Linnell for valuable help.

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[Received, December 11th, 1922.]

XXXVIII.—*Isolation of the Oxide of a New Element.*

By ALEXANDER SCOTT.

IN 1913 I had the opportunity of examining a black titaniferous iron sand from Maketu, New Zealand. This was found to consist almost exactly of 75 per cent. of magnetic iron oxide, Fe_3O_4 , and 25 per cent. of titanium dioxide, TiO_2 . The titanium dioxide on further examination was found to contain a minute amount of some similar substance which was not attacked or rendered soluble by the reagents which should dissolve both titanium and zirconium oxides. The original sand seemed to be entirely free from any of the "rare earths" and this residue possessed none of their characteristic properties.

Needless to say, work on this interesting substance was practically stopped during the war, but the accumulation of small quantities was carried on intermittently until a quantity of about 1·4 grams of a pale buff-coloured powder was collected in a fair state of purity.

Briefly, the method of isolating it from the original material was to boil the sand with concentrated sulphuric acid until all the black particles had disappeared, and pour the product into water, then dissolve the precipitated titanium dioxide in hot sulphuric acid; any undissolved residue was dried and fused with sodium bisulphate, the melt dissolved in water, and the new residue fused with pure caustic soda; the insoluble residue from this was again subjected to fusion with these reagents when, as above mentioned, 1·4 grams were separated and labelled "New oxide" in 1918. It had all the characteristics which one would expect in an oxide of the titanium-zirconium group and its double fluoride with potassium crystallised in a way very similar to the corresponding fluorides of titanium and zirconium.

All attempts to prepare soluble salts such as the sulphate, chloride, and nitrate, as might be anticipated, proved fruitless, so that no obvious method of determining the atomic weight of the element except by means of the double fluoride seemed feasible.

Two experiments with an impure sample of the double fluoride (which almost certainly contained excess of potassium fluoride and perhaps also some sodium fluoride) gave 144 for the atomic weight of the element.

I give the actual weighings in the first experiment:

Platinum crucible + K_2XF_6 dried at 135°	13·4438
after ignition with strong H_2SO_4 giving NO_2 + K_2SO_4	13·3893
Crucible + oxide after re-ignition with $(\text{NH}_4)_2\text{CO}_3$	13·2288
Crucible	12·9992

therefore 0·4446 of salt gave 0·2296 of oxide.

In a second experiment with another lot of the same sample 0.3306 of salt gave 0.1761 of oxide; hence 0.7752 of salt gave 0.4057 of oxide, that is, 52.3 per cent. of its weight of the oxide.

The zirconium double fluoride only gives 43.35 per cent.

The result above given is undoubtedly much too low because of the impurities indicated.

The oxide obtained from the double fluoride was of a cinnamon-brown colour; it is possible that the colour may be due to a trace of iron which still seems to be present in spite of the drastic treatment which the material has received.

I have offered to send my preparations for examination to Drs. Coster and Hevesy at Copenhagen, who are the discoverers by means of X-ray spectral analysis of lines corresponding to an element the atomic number of which is 72, and await their report with breathless interest. The examination with the appliances at their command, far more powerful and discriminating than any private investigator can possess, must be regarded as settling the question whether my "New Oxide" is, or contains, the oxide of Element number 72.

Should it prove to be so, as the new element belongs to the same family as titanium and is found along with it in the black sand, I propose to give it a name derived from *Oceanus*, one of the Titans. The name which I suggest is *Oceanium*, which has the further recommendation of recalling that the element comes from the sea-shore of New Zealand, one of the components of *Oceania*.

34, UPPER HAMILTON TERRACE,
LONDON.

[Received, February 1st, 1923.]

XXXIX.—*The Configuration of the Doubly-linked Ter-valent Nitrogen Atom. The Resolution of the Pyridylhydrazone of cycloHexylene Dithiocarbonate.*

By WILLIAM HOBSON MILLS and HANS SCHINDLER.

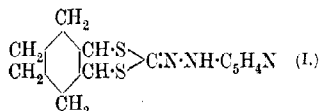
SOME years ago one of us, with Miss A. M. Bain (T., 1910, 97, 1866), examined the stereochemical relationships of the oxime of cyclohexanone-4-carboxylic acid (Perkin, T., 1904, 85, 416), with the object of obtaining information respecting the disposition in space of the valencies of the doubly-linked nitrogen atom, and showed that this compound could be obtained in two enantiomorphously related optically active forms.

Since it is impossible to account for the molecular asymmetry thus demonstrated if the valencies of the nitrogen atom in the

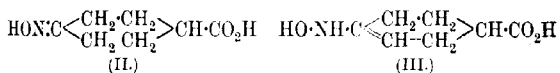
oximino-group in this compound have a planar distribution, direct evidence was provided that these valencies do not lie in one plane, but are directed along the three edges of a trihedral angle.

It was also shown (T., 1914, 105, 64) that the benzoylphenylhydrazone and the semicarbazone of *cyclohexanone-4-carboxylic acid* could be obtained in optically active forms and thus that, in these compounds also, the three valencies of the doubly-linked nitrogen atom are similarly asymmetrically disposed.

In view of the interest attaching to the stereochemistry of the doubly-linked nitrogen atom it has seemed to us desirable to investigate in a similar manner some other compound of as different a chemical type as possible from 4-oximinocyclohexanecarboxylic acid but possessing the same stereochemical characteristic that its molecule is asymmetric or not according as the three valencies of the doubly-linked nitrogen atom have a trihedral or a planar distribution. In the present communication, an account is given of the synthesis and resolution into optically active components of the pyridylhydrazone of *cyclohexylene dithiocarbonate* (I).



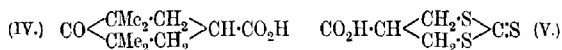
In discussing the optically active forms of the oxime of *cyclohexanonecarboxylic acid*, the question was considered whether their optical activity was possibly to be accounted for by the hypothesis that the optically active compounds obtained did not really contain the oximino-group, but were the *d*- and *l*-forms of a desmotope of the oxime, the hydroxylamine derivative (III).



It was pointed out, however, that the behaviour of the substance towards Fehling's solution showed clearly that it was a true oxime (II), and this was confirmed by the fact that the optical activity was more persistent in presence of caustic alkalis which, if tautomerism of the kind suggested were possible, would favour the acidic oximino-form, whilst acidification, which should increase the stability of the more basic hydroxylamino-form, caused an immediate disappearance of the activity.

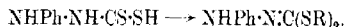
Nevertheless, in seeking another compound which could be employed for investigating the stereochemistry of nitrogen by

this method it seemed to us important to find one in which all possibility of passage by migration of a mobile hydrogen atom into a compound with an ordinary asymmetric carbon atom should be excluded. The most obvious modification of oximinocyclohexanecarboxylic acid by which this immobility could be secured would consist in the replacement of the four hydrogen atoms in the two methylene groups adjacent to the oximino-radicle by methyl groups, but there seemed little prospect that the problem could be solved in this way. For the carbonyl group in tetramethylcyclohexanonecarboxylic acid (IV) would be so surrounded



with methyl groups that it would probably prove indifferent, on account of steric hindrance, to hydroxylamine or to substituted hydrazines (Petrenko-Kritschenko, *Ber.*, 1896, **29**, 996; Bouveault and Loquin, *Bull. Soc. chim.*, 1906, [iii], **35**, 655). It appeared, however, that our object might be achieved by employing a compound containing, in place of the system $\text{-CMc}_2\text{CO} \cdot \text{CMc}_2\text{-}$, the radicle of the thiocarbonates $\text{-S} \cdot \text{CS} \cdot \text{S}-$. Mobile hydrogen is absent from this grouping and there was reason to believe that the thiocarbonyl radicle which it contains would show a capacity for condensing with phenylhydrazine similar to that of the carbonyl group in the ketones.

It is noteworthy that Busch and Lingenbrink (*Ber.*, 1889, **32**, 2620) were able, by alkylating phenyldithiocarbazinic acid, to prepare compounds which they regarded as phenylhydrazones of dithiocarbonic esters.



Moreover, Busch found (*Ber.*, 1901, **34**, 1119) that, in certain cases, when a compound of this type contained two different radicles, R and R', it could be obtained in two isomeric forms and he was further able to obtain evidence (*Ber.*, 1912, **45**, 75) in support of the view that the isomerism in question was stereoisomerism of the type suggested by Hantzsch and Werner.

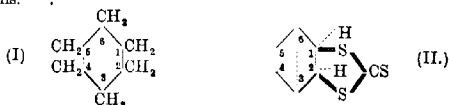
The trithiocarbonate corresponding, from this point of view, with cyclohexanonecarboxylic acid would be a compound of the formula V. It appeared preferable, however, in order to secure as great a difference as possible from the compounds previously investigated, as well as for practical reasons, to make the thiocarbonate radicle part, not of a six-membered, but of a five-membered ring, and to obtain the necessary stereochemical relationships by fusing this five-membered ring symmetrically with the cyclohexane ring.

We therefore undertook the preparation of *cyclohexylene* trithio-carbonate, $\begin{matrix} \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH} \cdot \text{S} \\ \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH} \cdot \text{S} \end{matrix} > \text{CS}$.

According to well-recognised stereochemical principles the planes * containing the two rings must intersect at an angle as shown in Fig. 1 (p. 318) (the third plane represented being that which contains the two tertiary hydrogen atoms) and the molecule must

* In these diagrams the six carbon atoms of the *cyclohexane* ring are represented for simplicity as lying in one plane. Since, however, the angle between the carbon-to-carbon valencies of a methylene group in an unstrained polymethylene chain is less than the angle of a regular hexagon, it is probable that this ring is actually somewhat distorted.

The configuration of *cyclohexane* was considered by Sachse (*Ber.*, 1890, 23, 1363; *Z. physikal. Chem.*, 1892, 10, 203), who pointed out that there are two arrangements of the carbon atoms in the *cyclohexane* ring in which it would be free from strain and which are therefore to be regarded as its normal configurations.



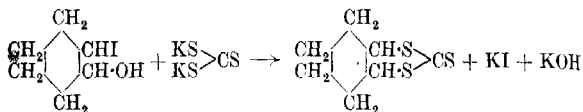
In both these arrangements four carbon atoms, in the relative positions 1, 2, 4, and 5, lie in one plane and the distortion of the ring by which the strain is relieved consists in the displacement of the other two carbon atoms, 3 and 6, to an equal distance to one side or the other of this plane. The first arrangement is that in which the carbon atoms are on opposite sides and the second that in which they are on the same side of the plane. A little consideration will show that when a second ring is fused with the *cyclohexane* ring, as is the case in *cyclohexylene* dithiocarbonate, the second of these arrangements alone is possible. The effect of this distortion on the *cyclohexylene* dithiocarbonate molecule (II) will therefore be that the carbon atoms 4 and 5 will not lie in the plane which contains the carbon atoms 1, 2, 3, and 6, but they will each be situated an equal distance behind it. Thus, in spite of this distortion of the *cyclohexane* ring, the plane through the lines *ao*, *bo*, *co* is still a plane of symmetry of the *cyclohexylene* dithiocarbonate molecule.

Sachse assumed that the natural angle between the carbon-to-carbon valencies in a chain of methylene groups was $109^\circ 28'$. The angle between carbon valencies can, however, only have this value in compounds in which the carbon atom is attached to four like atoms or groups. The angle in question is evidently greater than that in such fully symmetrical compounds (Ingold, T., 1921, 119, 305, estimates it from considerations based on atomic volumes as 115.3°), and thus it must approximate more closely to the angle of the regular hexagon than Sachse supposed. The degree of distortion of the *cyclohexane* ring from the plane configuration is therefore presumably comparatively slight.

Since the isomerism which distortions of this type, if sufficiently permanent, would condition among alicyclic compounds has never been observed, it is probably to be concluded that in liquid or dissolved substances they are in continuous flux and therefore cannot be the cause of optical activity.

possess a plane of symmetry, namely, the plane cutting the three planes shown in the figure at the dotted lines *ao*, *bo*, and *co*.

Unfortunately, it was found that the preparation of this compound presented very considerable difficulties. Whilst monocyclic esters of trithiocarbonic acid, such as ethylene trithiocarbonate (Husemann, *Annalen*, 1862, **123**, 83), or trimethylene trithiocarbonate, are easily obtained by the interaction of ethylene bromide or trimethylene bromide with sodium or potassium thiocarbonate, we were quite unable to obtain the dicyclic *cyclohexylene* ester from *cyclohexene* dibromide in this way. At length, however, after having tried several other methods, we found that the ester could be prepared, though not very readily, by the action of potassium thiocarbonate on 2-iodocyclohexanol, a compound discovered by Brunel (*Compt. rend.*, 1902, **135**, 1057).



As we had expected, it reacts readily with phenylhydrazine to give the phenylhydrazone, $\text{C}_6\text{H}_{10} \begin{array}{c} \text{S} \\ \diagup \quad \diagdown \\ \text{S} \end{array} > \text{C:N-NHPh}$.

If the valencies of the doubly-linked nitrogen atom in this compound are trihedrally disposed, it must consist of a mixture (or a racemic compound) of two enantiomorphous forms, but whether this was the case or not could not be determined on account of its chemical indifference.

To obtain a compound suitable for resolution, it was necessary to prepare a hydrazone with either acidic or basic properties. The optically active oxime of Mills and Bain was acidic. It was therefore preferable for the present purpose to employ a basic compound, the more so since the presence of an acidic group, such as a carboxyl or sulphonie group, in a hydrazine considerably diminishes its reactivity towards ketones. It seemed that basicity might be most easily conferred on this compound by replacing the phenyl group in the hydrazone residue by pyridyl; we therefore prepared 2-hydrazinopyridine described by Fargher and Furness (*T.*, 1915, **107**, 688) and found that this reacted with *cyclohexylene* trithiocarbonate, although considerably less readily than phenylhydrazine, giving the pyridylhydrazone of *cyclohexylene* dithiocarbonate. This had marked basic properties and thus a compound presenting the necessary chemical and stereochemical characteristics was finally obtained.

In studying the salts which this pyridylhydrazone formed with

dilute acids, we examined first the *d*-bromocamphorsulphonate and found at once that by means of this salt a resolution could be effected. After crystallising the *d*-bromocamphorsulphonate from alcohol and ether and decomposing it with ammonia, a specimen of the hydrazone was obtained which showed marked levorotation, $[\alpha]_D^{18} - 53^\circ$ in carbon disulphide solution. However, in the next resolution which was carried out the first crop of salt gave a dextro-rotatory specimen of the hydrazone on decomposition, and subsequent experiments showed that the behaviour of the salt on fractional crystallisation was exceedingly erratic.

As initially prepared, by combining the hydrazone with the acid in alcoholic solution and precipitating the greater part of the product with ether, the salt showed a specific rotation $[\alpha]_D$ in alcoholic solutions of from $+55^\circ$ to $+58^\circ$. On dissolving this salt in alcohol and causing it to crystallise in fractions by the addition of successive quantities of ether, the first fraction sometimes showed an increased specific rotation, for example, in one case $[\alpha]_D + 80^\circ$, but on the other hand the first fraction would very frequently show a diminished specific rotation, often of only $+45^\circ$ or less, and the second fraction would then generally show a specific rotation higher than that of the initial product.

A similar behaviour was shown by the fractions when recrystallised. Whether the fraction was one of lower or of higher specific rotation than the initial product, the first crop obtained in the recrystallisation might show either an increased or a diminished specific rotation, and inoculation seemed without effect. The salt recovered from the final mother-liquors in the recrystallisation was, however, in most cases of low specific rotation, $[\alpha]_D + 10^\circ$ to -14° .

Since the process was thus so little subject to control, we fractionated the salt by precipitation by ether from alcoholic solution and kept all fractions of which the specific rotation was either higher than $[\alpha]_D + 67^\circ$ or lower than $[\alpha]_D + 36^\circ$. The strongly rotatory fractions were united, as were also the feebly rotatory fractions, and in this manner two quantities of the salt were accumulated of mean specific rotation $[\alpha]_D + 82^\circ$ and $[\alpha]_D + 8.6^\circ$, respectively.

Each of these quantities was decomposed with ammonia and the optically active hydrazone liberated was recrystallised. Each of the two specimens thus obtained had a melting point about half a degree higher than that of the inactive compound and was shown by combustion to be the analytically pure pyridylhydrazone. The pure hydrazone isolated in this way from the salt of higher specific rotation was strongly dextrorotatory, showing a specific

rotation $[\alpha]_D + 46^\circ$, whilst that from the salt of lower specific rotation was considerably more strongly levorotatory ($[\alpha]_D - 83^\circ$).*

Thus although the peculiar behaviour of the salt on recrystallisation prevented us from obtaining, with the quantity of material at our disposal, the enantiomerides in optical purity, these observations prove conclusively that the hydrazone exists in two enantiomorphous forms. Its molecule therefore possesses no plane of symmetry.

Now it will be clear that when the residue of *cyclohexylene* dithiocarbonate, $C_6H_{10} \begin{smallmatrix} S \\ \diagup \diagdown \\ C \end{smallmatrix} < S > C <$, is united with the pyridylhydrazine residue, $>N \cdot NHPy$, to form the pyridylhydrazone, if the disposition of the three valencies of the doubly-linked nitrogen atom in the latter compound is such that they lie in one plane, this plane must

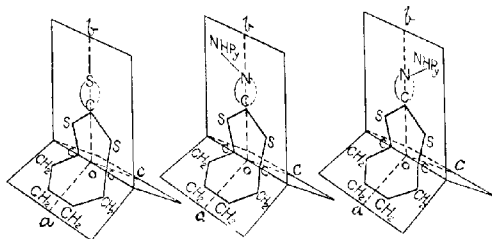


FIG. 1.

FIG. 2a.

FIG. 2b.

coincide with the plane of symmetry of the *cyclohexylene* dithiocarbonate residue. The doubly-linked nitrogen atom as well as the nitrogen atom of the pyridylamino-radicle will then lie in this plane, and therefore it will be a plane of symmetry of the whole molecule, and the molecule must be superposable upon its mirror image. But, as has been shown, the hydrazone exists in two enantiomorphously related modifications. The pyridylamino-radicle therefore cannot lie in the plane of symmetry of the *cyclohexylene* dithiocarbonate residue, but must be permanently displaced either to one side of it or the other, somewhat as represented in Figs. 2a and 2b. The resolution of the hydrazone into

* The optically pure enantiomerides probably possess considerably larger specific rotations. A specimen of salt of specific rotation $[\alpha]_D + 136^\circ$ gave a specimen of hydrazone of specific rotation $[\alpha]_D + 131^\circ$ and another specimen of salt of specific rotation $[\alpha]_D - 3^\circ$ gave a specimen of hydrazone of specific rotation $[\alpha]_D - 100^\circ$.

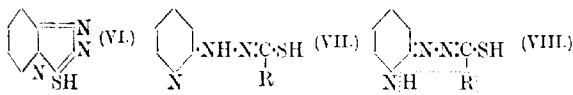
The amounts of these products obtained were insufficient for analysis, but in view of the results described above there is no reason to doubt that the active material in each case consisted of analytically pure hydrazone.

optically active enantiomerides thus constitutes a direct proof that the three valencies of the doubly-linked nitrogen atom, which the molecule of this compound contains, do not lie in one plane but are directed along the three edges of a trihedral angle.

These observations, taken together with those of Mills and Bain on the oxime, the benzoylphenylhydrazone, and the semicarbazone of cyclohexanecarboxylic acid, thus show that in several different types of compounds the valencies of a doubly-linked nitrogen atom have a trihedral disposition. They accordingly provide a direct proof of the fundamental hypothesis on which Hantzsch and Werner based their explanation of the isomerism of the oximes and other compounds containing a similarly bound nitrogen atom.

In one respect, the pyridylhydrazone of cyclohexylene dithiocarbonate shows a marked difference from the oxime and the hydrazones of cyclohexanecarboxylic acid. The latter substances are exceedingly sensitive to acids, losing their activity immediately on acidification. This hydrazone was found, however, to retain its activity even after keeping for hours in solution in dilute hydrochloric acid. At the same time, it possesses no great stability, for in working up the mother-liquors of the bromocamphorsulphonate a peculiar odour, evidently proceeding from small quantities of a decomposition product, was frequently noticed.

The trithiocarbonate is also easily decomposed. When it was heated in alcoholic solution with pyridylhydrazine in order to prepare the pyridylhydrazone, a by-product of markedly acidic character was always formed. This had a composition corresponding with the formula $C_6H_5N_3S$ and it was easily obtained by heating pyridylhydrazine with potassium trithiocarbonate and acetic acid. It was thus evidently a mercaptan (VI) derived from benzoisotriazole, a condensed ring system formed by fusion of a dihydropyridine nucleus with a triazole nucleus, discovered by Marckwald and Rudzik (*Ber.*, 1903, 36, 1111).



A similar compound was obtained by Marckwald and Meyer from 2-quinolyldiazine (*Ber.*, 1900, 33, 1888). Moreover this substance shows the behaviour characteristic of compounds containing the group $HS-C \begin{smallmatrix} \nearrow N \\ \nwarrow N \end{smallmatrix}$, first observed by Wohl and Marckwald (*Ber.*, 1889, 22, 576), in that the sulphhydryl radicle is very readily eliminated by warming with dilute nitric acid, benzoiso-

triazole being formed. This mercaptan probably owes its formation to the intermediate production of the tautomeric modification (VIII) of a pyridylhydrazone (VII).

EXPERIMENTAL.

cycloHexylene Trithiocarbonate.—2-Iodocyclohexanol was prepared by treating cyclohexene in ethereal solution with iodine in presence of yellow mercuric oxide and water (Brunel, *Compt. rend.*, 1902, 135, 1055). The crystalline product of the reaction was drained from adherent oil on unglazed tiles and recrystallised from light petroleum. This compound was converted into trithiocarbonate by heating the pure substance, melting at 41–42° (4.4 grams) for one and a half hours on the boiling water-bath with potassium trithiocarbonate (3.6 grams; 1 mol.) and aqueous methyl alcohol (32 c.c. of methyl alcohol and 12 c.c. of water).

The liquid, which at first was turbid, soon cleared, and cyclohexylene trithiocarbonate separated in yellow prisms. After cooling, the ester was collected and purified by recrystallisation from alcohol. It melts at 165–166° and is easily soluble in hot alcohol or carbon disulphide, but dissolves less readily in ether (Found: C = 44.0; H = 5.3; S = 50.6. $C_6H_{10}S_3$ requires C = 44.2; H = 5.3; S = 50.5 per cent.). The yield of the recrystallised product is usually only about 11 per cent. of that theoretically obtainable, the main product of the reaction being a viscous oil.

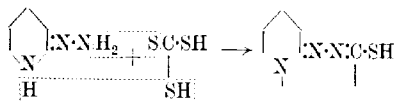
Phenylhydrazone of cycloHexylene Dithiocarbonate (cycloHexylene Phenylldithiocarbazine).—This compound is easily prepared by heating the trithiocarbonic ester on the boiling water-bath with an excess of phenylhydrazine (3.5 mols.) in alcoholic solution, hydrogen sulphide being eliminated. Better yields (about 87 per cent. of the theoretical) were obtained by heating the trithiocarbonic ester with phenylhydrazine hydrochloride (10 mols.) and sodium acetate (16 mols.) in aqueous alcoholic solution on the water-bath. On cooling, the phenylhydrazone crystallised in colourless leaflets, which, after recrystallisation from alcohol, melted at 181.5–182° (Found: C = 59.2; H = 6.0; N = 10.8; S = 24.1. $C_{13}H_{16}N_2S_2$ requires C = 59.0; H = 6.1; N = 10.7; S = 24.2 per cent.).

2-Pyridylhydrazone of cycloHexylene Dithiocarbonate (cycloHexylene 2-Pyridylldithiocarbazine).—The trithiocarbonic ester (1 gram) and an equal weight of 2-pyridylhydrazine (Fargher and Furness, *loc. cit.*) were dissolved in alcohol and boiled for seven hours on the water-bath. The greater part of the solvent was then evaporated and the crystals which separated on cooling were recrystallised twice from carbon disulphide and then once from alcohol. The pyridylhydrazone was thus obtained as a yellow, crystalline powder

melting at 167–168.5° and easily soluble in carbon disulphide or in hot alcohol (Found: C = 54.3; H = 5.8; N = 15.8; S = 24.4. $\frac{1}{12}\text{H}_{15}\text{N}_3\text{S}_2$ requires C = 54.4; H = 5.7; N = 15.9; S = 24.2 per cent.).

Benzoisotriazolyl Mercaptan.—This compound can be isolated from the alcoholic mother-liquor from which the crude pyridylhydrazine has crystallised by evaporating the alcohol and treating the residue with excess of aqueous ammonia. This dissolves the mercaptan (which contains the acidic grouping $\cdot\text{N}\cdot\text{C}\cdot\text{SH}$), but leaves the other substances present undissolved. The ammoniacal solution is filtered from these and acidified with acetic acid, when the mercaptan is slowly deposited. It is collected after two days, decolorised with animal charcoal, and recrystallised several times from hot water. It crystallises in fine, colourless needles and melts at 205–206°. It is very easily soluble in alcohol or in hot water, and is moderately soluble in ether or carbon disulphide. It is sufficiently strongly acidic to decompose sodium bicarbonate (Found: C = 47.7; H = 3.6; N = 27.0; S = 21.3. $\text{C}_6\text{H}_5\text{N}_3\text{S}$ requires C = 47.7; H = 3.3; N = 27.8; S = 21.2 per cent.).

This mercaptan is easily prepared by the action of trithiocarbonic acid on pyridylhydrazine.



Equimolecular quantities of pyridylhydrazine and potassium trithiocarbonate were boiled for two hours in alcohol to which a little glacial acetic acid had been added. The alcohol was then evaporated and the residue was dissolved in hot water. The mercaptan crystallised on cooling and was found to be identical with that obtained as a by-product in the preparation of the pyridylhydrazine.

The mercaptan was oxidised to benzoisotriazole by heating with excess of 20 per cent. nitric acid on the water-bath. A somewhat vigorous reaction took place with the evolution of nitrous fumes. On evaporating the nitric acid, the benzoisotriazole was left as a hygroscopic residue as described by Fargher and Furness (*loc. cit.*, p. 695). The *chloroplatinate* was precipitated at once on the addition of chloroplatinic acid to the aqueous solution of the base. It did not melt at 300° [Found: Pt = 29.7. $(\text{C}_6\text{H}_5\text{N}_3)_2, \text{H}_2\text{PtCl}_6$ requires Pt = 30.1 per cent.].

Resolution of cycloHexylene Dithiocarbonate Pyridylhydrazone.

The *d*-bromocamphorsulphonate, with the aid of which the resolution was effected, was prepared by adding a solution of *d*-bromocamphorsulphonic acid (0.64 gram) in absolute alcohol (2 c.c.) at the ordinary temperature to the hydrazone (0.5 gram; 1 mol.) in suspension in absolute alcohol (6 c.c.). After the hydrazone had passed into solution, which quickly took place, anhydrous ether (30–50 c.c.) was gradually added. Small crystals of the salt soon appeared and in a short time the greater part of the product separated as a voluminous, crystalline precipitate. When left in contact with the solution, the fine needles generally underwent a gradual transformation into larger crystals.

In this manner 4 grams of the hydrazone gave 8 grams of salt, the theoretical quantity being 8.7 grams. The specific rotation, $[\alpha]_D$, of different preparations varied from $+55^\circ$ to $+58^\circ$ in alcoholic solution.

To recrystallise the bromocamphorsulphonate, it was dissolved in the minimum quantity of absolute alcohol and anhydrous ether was added, when the salt was gradually precipitated in very fine needles. The second and subsequent crops were obtained by evaporating the mother-liquors to small volume in a vacuum at the ordinary temperature and then adding more ether.

The following examples, in which, however, less irregularity is apparent in the changes of specific rotation than was frequently observed, illustrate the behaviour of the salt on recrystallisation.

(1) 2.14 Grams of the salt as initially obtained gave, on being fractionated in the way described, a first fraction, weighing 0.41 gram, of specific rotation $[\alpha]_D + 48^\circ$, a second fraction, weighing 1.18 grams, of specific rotation $[\alpha]_D + 59^\circ$, and a third, weighing 0.32 gram, also of specific rotation $[\alpha]_D + 59^\circ$. The first and third fractions were worked up with others of similar specific rotation. The second was recrystallised separately and gave 0.94 gram of specific rotation $[\alpha]_D + 70^\circ$, which, again recrystallised, gave 0.73 gram of specific rotation $[\alpha]_D + 92^\circ$. All specific rotations were taken in alcoholic solution. Here a progressive elimination of the *l*-hydrazone *d*-bromocamphorsulphonate and a corresponding concentration of the *d*-hydrazone *d*-bromocamphorsulphonate was clearly taking place.

(2) A fraction, weighing 1.39 grams, of specific rotation $[\alpha]_D + 51^\circ$ was recrystallised and gave a first crop, weighing 0.88 gram, of specific rotation $[\alpha]_D + 32^\circ$ and a small second crop (0.05 gram) of specific rotation $[\alpha]_D + 71^\circ$. The first crop, thrice recrystallised, gave first 0.75 gram of specific rotation $[\alpha]_D + 26^\circ$, then 0.49 gram

of specific rotation $[\alpha]_D + 19^\circ$, and then 0.27 gram of specific rotation $[\alpha]_D - 3^\circ$. Thus in this example a concentration of the l-hydrazone *d*-bromocamphorsulphonate was being effected.

The way in which two fractions of salt of specific rotation $[\alpha]_D + 82^\circ$ and $[\alpha]_D + 8.6^\circ$, respectively, were obtained has already been indicated. These were investigated in the following manner.

A quantity of 2.07 grams of the salt of higher specific rotation was suspended in water and was decomposed by the addition of an excess of dilute ammonia. The hydrazone thus set free, being insoluble, was collected and, after having been dried, was recrystallised, first from carbon disulphide, and then from alcohol. This purification was accompanied by considerable loss, as the hydrazone is rather easily soluble in carbon disulphide, 0.44 gram only of hydrazone being obtained out of the theoretical quantity of 0.95 gram.

The specimen of hydrazone thus isolated melted sharply at $168-169^\circ$ (the inactive hydrazone melts at $167-168.5^\circ$) and was analytically pure (Found: C = 54.5; H = 5.7. Calc., C = 54.4; H = 5.7 per cent.). It was markedly dextrorotatory.

0.2064 Gram of hydrazone, in carbon disulphide solution (20 c.c.), gave $\alpha_D^{20} + 1.05^\circ$ ($l = 2.2$); whence $[\alpha]_D^{20} + 46.3^\circ$.

0.0617 Gram of hydrazone, in alcoholic solution (20 c.c.), gave $\alpha_D^{20} + 0.31^\circ$ ($l = 2.2$); whence $[\alpha]_D^{20} + 46^\circ$.

The hydrazone similarly isolated from the salt of specific rotation $[\alpha]_D + 8.6^\circ$ was strongly levorotatory. The quantity of this salt taken was 0.761 gram. The hydrazone obtained by decomposing it with ammonia after recrystallisation first from carbon disulphide and then from alcohol weighed 0.16 gram. It melted at $168-169^\circ$ and was analytically pure (Found: C = 54.6; H = 5.7. Calc., C = 54.4; H = 5.7 per cent.). It was examined polarimetrically with the following result.

0.0338 Gram, in alcoholic solution (10 c.c.), gave $\alpha_D^{20} - 0.28^\circ$ ($l = 1$); whence $[\alpha]_D^{20} - 83^\circ$.

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[Received, January 17th, 1923.]

XL.—*The Sorption of Iodine by Carbons Prepared from Carbohydrates.*

By JAMES BRIERLEY FIRTH.

THE work of investigators on sorption by carbon has hitherto been mainly confined to carbons of either animal or vegetable origin, such as bone charcoal, blood charcoal, or the different

varieties of wood and nut charcoal. The exception seems to have been sugar carbon, and to a lesser degree lampblack. It would appear that if carbons of different molecular complexity could be prepared, they would have a corresponding variation in activity and sorptive capacity.

The object of this series of investigations is to determine, if possible, whether the complexity and nature of the original compound influence the activity of the carbon produced from it, and also to determine the influence (if any) of such elements as nitrogen, sulphur, and the halogens in the parent substance. It is therefore proposed to prepare carbons from pure substances belonging to the various classes of organic compounds.

The present investigation is confined to carbons prepared from carbohydrates.

EXPERIMENTAL.

The chloroform was dried for several days over calcium chloride and fractionated, the middle portion only being taken.

Resublimed iodine was employed as solute.

The carbohydrates used were the purest obtainable, and those marked K were Kahlbaum's preparations. The carbohydrates were carbonised at as low a temperature as possible and the conditions were as nearly as possible the same in all cases. The resulting carbon was finely powdered, digested with concentrated hydrochloric acid, washed with water, and finally boiled with water until free from chloride, and the purity of the carbon then determined. Cellulose carbon was prepared from the best surgical cotton wool. It was digested successively with dilute potash, dilute hydrochloric acid, water, alcohol, and ether to remove admixtures and finishing materials. It was then carbonised as in other cases. A specimen of sugar carbon was prepared by adding concentrated sulphuric acid to a concentrated sugar solution, the resulting carbon was repeatedly digested and washed with boiling water until free from sulphate, and then treated as in other cases. The approximate density of each carbon was determined by the water displacement method. Although the values for density are not to be regarded as absolute, the figures indicate satisfactorily the relative densities of the various carbons.

N/10-Solutions of iodine in chloroform were used throughout. The carbon was heated to a dull red heat, out of contact with the air, immediately before being used. One gram of the finely divided carbon was used in each case and treated with 25 c.c. of the *N/10* iodine solution. The experimental details were very similar to those already stated (Firth, *Trans. Faraday Soc.*, 1921, 16, 434).

TABLE I.

Carbon prepared from	Percentage ash as prepared.	Percentage ash after purification.	Density.	Remarks.
Sucrose by heat }	0.245	0.086	1.501	{ Bright; easily powdered
Sucrose by H_2SO_4 }	0.773	0.189	1.700	"
Glucose	1.784	0.512	1.502	"
Maltose (K)	0.111	0.098	1.509	"
Lactose (K)	0.637	0.372	1.619	"
Lævulose (K)	0.323	0.129	0.410	"
Wheat starch }	0.504	0.461	1.434	{ Dull; easily powdered
Potato starch }	2.810	1.326	1.515	"
Rice starch }	2.770	1.036	1.436	{ Fine black powder, easily pyrophoric
Dextrin (K)	0.661	0.432	1.497	{ Bright; easily powdered
Inulin (K)	2.071	1.117	1.506	{ Very hard; difficult to powder
Cellulose	0.486	0.301	1.480	{ Very fine powder, easily pyrophoric

The temperature of experiment was 18° . The results are expressed in terms of 100 c.c. of solution; the mass of carbon, m , = 4 grams; x/m = grams of iodine sorbed by 1 gram of carbon; $a - x$ = the final concentration of the solution in grams per 100 c.c. The time of exposure of the carbon to the solution was varied from five minutes to seven days. The results are given in Table II.

From Table I, the purest carbon of the series is seen to be that prepared from maltose, whilst potato starch carbon finally contained the highest percentage of ash. With three exceptions, the ash was considerably less than 1 per cent., whilst in two cases it was less than 0.1 per cent. During carbonisation, most carbohydrates passed through a very viscous phase and gave rise to a friable, metallic-looking carbon mass. In the cases of rice starch and cellulose, no such phase occurred, and the ultimate product was a very fine, easily pyrophoric powder, whilst inulin gave rise to a dull and exceedingly hard carbon.

From Table II it will be observed that the various carbons differ very much in *activity*. The values of x/m for an interval of five minutes vary from 0.06672 in the case of lævulose carbon to 0.2917

TABLE II.

Source of carbon.	Time.	x/m .	$a-x$.	Source of carbon.	Time.	x/m .	$a-x$.
Sucrose (by heat)	5 mins.	0.2439	0.2941	Dextrin	5 mins.	0.1562	0.6450
	30 "	0.2540	0.2537		30 "	0.1647	0.6110
	2 hours	0.2622	0.2209		2 hours	0.1803	0.5486
	24 "	0.2847	0.1309		24 "	0.1981	0.4774
	3 days	0.2958	0.0865		3 days	0.2149	0.4102
	7 "	0.3085	0.0357		7 "	0.2303	0.3246
Sucrose (by H_2SO_4)	5 mins.	0.1859	0.5261	Cellulose	5 mins.	0.2911	0.1050
	30 "	0.1961	0.4853		30 "	0.2942	0.0930
	2 hours	0.2136	0.4153		2 hours	0.2963	0.0846
	24 "	0.2289	0.3541		24 "	0.3006	0.0674
	3 days	0.2631	0.2173		3 days	0.3073	0.0406
	7 "	0.2762	0.1649		7 "	0.3106	0.0274
Glucose	5 mins.	0.2917	0.1019	Potato starch	5 mins.	0.2858	0.1265
	30 "	0.2954	0.0881		30 "	0.2892	0.1129
	2 hours	0.2979	0.0781		2 hours	0.2931	0.0973
	24 "	0.3012	0.0649		24 "	0.2969	0.0821
	3 days	0.3092	0.0329		3 days	0.3047	0.0509
	7 "	0.3104	0.0281		7 "	0.3098	0.0305
Maltose	5 mins.	0.1951	0.4893	Rice starch	5 mins.	0.2346	0.3313
	30 "	0.2025	0.4597		30 "	0.2483	0.2765
	2 hours	0.2142	0.4129		2 hours	0.2587	0.2349
	24 "	0.2429	0.2981		24 "	0.2692	0.1929
	3 days	0.2868	0.1225		3 days	0.2878	0.1185
	7 "	0.3012	0.0649		7 "	0.2998	0.0705
Lactose	5 mins.	0.1734	0.5762	Wheat starch	5 mins.	0.2301	0.3494
	30 "	0.1841	0.5334		30 "	0.2456	0.2874
	2 hours	0.1952	0.4890		2 hours	0.2532	0.2570
	24 "	0.2270	0.3618		24 "	0.2699	0.1902
	3 days	0.2680	0.1978		3 days	0.2868	0.1226
	7 "	0.2996	0.0714		7 "	0.2987	0.0750
Lævulose	5 mins.	0.06672	1.0029	Inulin	5 mins.	0.1698	0.5906
	30 "	0.07854	0.9556		30 "	0.1827	0.5390
	2 hours	0.09364	0.8952		2 hours	0.2001	0.4694
	24 "	0.1328	0.7386		24 "	0.2192	0.3930
	3 days	0.1545	0.6518		3 days	0.2352	0.3290
	7 "	0.1741	0.5734		7 "	0.2581	0.2374

in the case of glucose carbon, and for twenty-four hours the values are 0.1328 and 0.3012, respectively. It will be observed from Table I that lævulose has the lowest density of the series, but the results in general do not indicate that density is a primary factor in determining the activity of the carbon. Glucose, cellulose, and potato starch carbons show very high activity, and with the exception of lævulose the remainder of the carbons are of medium activity.

After a period of seven days, the total iodine sorbed by the respective carbons appears to be approaching an identical value; that is, ultimately the sorptive capacity in all cases will be the same. In order to test this view, the three carbons from glucose,

lævulose, and dextrin, under the same conditions as before, were exposed to the iodine solution for six months; the x/m values then were: glucose 0.3128, lævulose 0.2893, dextrin 0.2962. These results would indicate, therefore, that under the conditions of the present experiments the ultimate sorptive capacities of the carbons of this series are the same.

Summary.

For the conditions of the experiments as herein described:

1. The *activity* of the carbons prepared from carbohydrates may vary over quite a large range.
2. The greatest activity is displayed by the carbon prepared from glucose, and the least by the carbon prepared from lævulose.
3. The ultimate sorptive capacity of all the carbons prepared is the same.

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[Received, December 16th, 1922.]

XLI.—*The Chemistry of the Glutaconic Acids. Part XIV. Three-carbon Tautomerism in the cyclo-Propane Series.*

By FRANK ROBERT GOSS, CHRISTOPHER KELK INGOLD, and
JOCELYN FIELD THORPE.

THE outcome of work, which has been carried out on glutaconic acid and its derivatives during the past seventeen years, has been to show that the ordinary geometrical conceptions regarding the influence of the double bond fail to account for the peculiar reactions of these substances, excepting in the case of acids in which the last remaining mobile hydrogen atom has been replaced by an alkyl group, for instance, $\alpha\alpha$ -dimethylglutaconic acid and $\alpha\alpha\beta$ -trimethylglutaconic acid, which cease to be of interest from the point of view of three-carbon tautomerism, and are found to occur in ordinary *cis*- and *trans*-modifications, the former alone being capable of yielding an anhydride. Glutaconic acid, on the other hand, in spite of frequent attempts, has been isolated in only one form; and this form, instead of being of the usual stable *trans*-configuration, possesses a *cis*-structure, since it yields an anhydride very readily. It is true that many of the alkyl-substituted glutaconic acids which still contain a mobile hydrogen atom exist in two modifications, but the isomerism here is certainly not of the ordinary geometrical

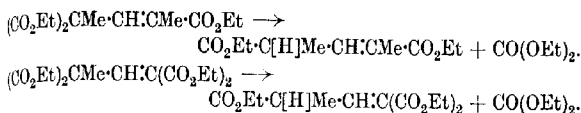
type, since, unlike $\alpha\alpha$ -dimethylglutaconic acid and other acids of the non-mobile series, the isomerides give anhydrides with equal ease. Only when the mobile hydrogen atom is replaced, or when the mobility is reduced by the presence of bulky substituents, as in the case of β -phenyl- α -methylglutaconic acid, does ordinary geometrical isomerism occur.

In the mobile series, therefore, the static geometrical conception must be replaced by a broader view, and one of the principal results of recent work has been to confirm the view, advanced by Thole and Thorpe (T., 1911, 99, 2187), that these acids are mobile tautomeric substances, and that the α - and γ -carbon atoms of the three-carbon system function equally. A striking and most welcome additional confirmation is provided by the recent experiments of Feist (*Annalen*, 1922, 428, 25 *et seq.*), who found that asymmetrically substituted glutaconic esters, on fission by the ozone method, gave, not the two products expected from a static substance having the double bond in a definitely fixed position, but four products, two of which corresponded with each of the two possible positions for the double bond. This kind of behaviour appears to be peculiar to all symmetrical mobile systems, since not only glutaconic esters, but also diazoamino-compounds and amidines, yield four products instead of two when subjected to fission by suitable reagents (Ingold and Piggott, T., 1922, 121, 2381).

The idea of symmetry is not conveyed by the ordinary double-bonded formula of the glutaconic acids, and it has been customary to employ the "semi-aromatic" mode of formulation, which is intended to express, not only the symmetry of the mobile system, but also its stability and the strong tendency to its formation. Thus it has repeatedly been shown that acids, to which semi-aromatic formulæ have been given, are only with the greatest difficulty reduced to the corresponding glutaric acids, whilst the esters show little or no tendency to form additive products with ethyl cyanoacetate in the normal manner characteristic of $\alpha\beta$ -unsaturated esters. In other words, the appearance of mobility in the glutaconic acids is associated with a definite loss of additive power, to which further reference will be made below.

The other point, which has frequently been emphasised, is the remarkable tendency to the formation of the mobile glutaconic acids, which is such that groups, for instance the carbethoxyl group, are removed with quite extraordinary ease, and in the presence of reagents which do not usually effect their elimination, when the mobile hydrogen atom necessary for glutaconic tautomerism can thereby be acquired. Thus although ethyl α -carboxyglutaconate and ethyl $\alpha\gamma$ -dicarboxyglutaconate are both quite stable towards

sodium ethoxide, ethyl α -dimethyl- α -carboxyglutaconate and ethyl α -methyl- α -dicarboxyglutaconate, on treatment with cold sodium ethoxide, readily split off a carbethoxyl group as ethyl carbonate, and thus acquire the hydrogen atom necessary for tautomerism (Bland and Thorpe, T., 1912, **101**, 871):



Similar examples have been described in the case of certain indene derivatives (Ingold and Thorpe, T., 1919, **115**, 143) which are analogous to glutaconic acid, and there is every reason to suppose that the phenomenon is fundamentally identical with the formation of mobile keto-enol systems, by the elimination of a bromine atom as hypobromous acid in the presence of dilute alkalis (Norris and Thorpe, T., 1921, **119**, 1202). Such abnormal reactions appear to be peculiar to the formation of mobile tautomeric systems, and represent a feature of which count must be taken in arriving at a just appreciation of the molecular condition of these substances.

For these reasons, it seemed desirable to investigate the behaviour of certain cyclic substances possessing a structure similar to that of glutaconic acid, in order to ascertain whether the phenomena associated with this particular group are of widespread occurrence. The substance which first suggested itself was the *cyclopropene* acid (I), which, if formulated as a glutaconic acid, would have the structure (II) possessing an axis of trigonal symmetry, the mobile hydrogen atom belonging equally to each of the three carbon atoms composing the ring:



Such a substance would doubtless possess quite extraordinary stability and exhibit to a marked degree the loss of additive power which appears in every case to accompany the production of a symmetrical glutaconic structure.

Pending, however, a study of the conditions under which this acid could be prepared in quantity from tricarballic acid, it was decided to carry out investigations on the chemistry of acids of the type III and VI, in order to ascertain whether they fall within the glutaconic conception and possess in reality formula IV.



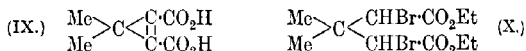
Now it is a curious fact that cyclopropene acids of type III or VI are easily prepared, so long as there is a hydrogen atom available to enable them to assume the structure of formula IV. Thus Farmer and Ingold (T., 1921, 119, 2003) were able to prepare the acid (VI) from the bromoglutaconic ester (V)



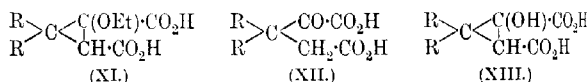
whilst, by a similar process, Feist (*Ber.*, 1893, 26, 750) obtained the acid (VIII) from bromoisodehydraetic ester (VII).



But in every case in which attempts have been made to prepare acids of this constitution without the hydrogen atom, for example, the acid (IX), other products have been formed.



The first attempts of this kind were made by Perkin and Thorpe (T., 1901, 79, 732), who treated the dibromo-ester (X) with alcoholic potassium hydroxide and obtained the ethoxy-derivative (XI), whilst from the corresponding dibromo-acid they obtained the keto-acid (XII). It was suggested at the time, that in all probability the unsaturated ring acid was first formed, but that, being unstable, it added on either the elements of alcohol to form the ethoxy-derivative, or of water to form the keto-acid.



Since that time the behaviour of other dibromo- $\beta\beta$ -substituted glutaric acids has been studied, with results which are summarised briefly in the following table.

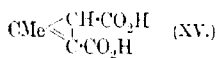
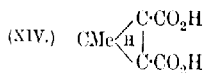
$\alpha\alpha'$ -Dibromoglutaric ester with $\beta\beta$ -group.	Products of action of alcoholic KOH.	Type.	Observers.
Dimethyl	Ethoxy-ring acid	XI	Perkin and Thorpe
	Keto-acid	XII	(<i>loc. cit.</i>).
Methyl ethyl	Ethoxy-ring acid	XI	Singh and Thorpe, this
	Keto-acid	XII	vol., p. 113.
Diethyl	Hydroxy-ring acid and keto-acid in equilibrium	XIII	Deshapanda and Thorpe
		XII	(T., 1922, 121, 1430).
cycloHexane	Hydroxy-ring acid only	XIII	Beesley, Ingold, and Thorpe (T., 1915, 107, 1080).

It will be noticed that the order of stability of the *cyclopropane* ring is in accordance with our general view of the influence of groups and ring-systems on the deflection of the tetrahedral angle, and that, for example, the *cyclohexane* complex, which produces the greatest effect, renders the hydroxy-ring stable; whereas in the case of the diethyl group the slight alteration of the angle leads to tautomerism between the open-chain keto-acid and the hydroxy-ring acid; in the other two instances, the angular deflection is not sufficient to render the ring structure stable, unless an ethoxy-group is attached to one of the carbon atoms.

From this evidence it seems fairly certain that in every case the products are due to the initial formation of the unsaturated ring structure (type IX), and that in no single instance does this structure possess sufficient stability to enable it to survive, in spite of the fact that *gem*-groupings should favour its stability. Moreover, the replacement of one of the alkyl groups of the *gem*-complex by hydrogen should, owing to the consequent increase of the tetrahedral angle (Ingold, T., 1921, 119, 305; 1922, 121, 2676) decrease the stability of the unsaturated ring, whereas, actually, the contrary is the case to such a degree, that the unsaturated systems (VI) and (VIII) are not only capable of existence, but are comparatively stable substances.

It is evident, therefore, that in the systems conventionally represented by formulæ (VI) and (VIII), conditions are present which are not accounted for by the ordinary conceptions applicable to these structures, and that these conditions are determined by the presence of a mobile hydrogen atom, the acids being in every way comparable with glutaconic acid in the possession of what we have named elsewhere "semi-aromatic" character.

Strong confirmation of this is obtained on considering the properties of the substances themselves. Thus the acid previously represented by formula (VIII) occurs, like glutaconic acid, in one form only (m. p. 200°), which must therefore have the "normal" structure (XIV), although in solution there must be a definite phase consisting of the "labile" form (XV), since many of the reactions of the substance are obviously reactions of this form.

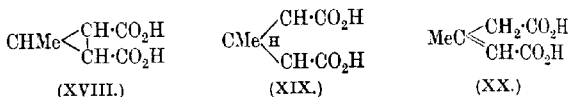


Moreover, although only one acid is isolable, it forms both normal and labile esters. Further details of the relationship between these two esters will be given below, but it may be added here that additional evidence of the labile phase of the acid is shown by its

conversion (in poor yield) into its hydroxy-anhydride (XVI), which must take place through the intermediate formation of the labile modification, and by the formation of 2:3-dibromo-3-methylcyclopropane-1:2-dicarboxylic acid (XVII) on addition of bromine.

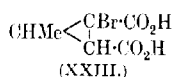
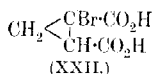
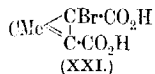


Nevertheless the only acid which can be isolated is an extremely stable substance, which sublimes without decomposition at temperatures approaching 200°, and, like all true glutaconic acids, is very stable towards reducing agents, since it remains quite unattacked on prolonged treatment with sodium amalgam, even in boiling solution. It can, however, be reduced by heating with hydriodic acid under energetic conditions, but the remarkable point is that the glutaconic system is not reduced to a glutaric acid system by this means, since no trace of the saturated cyclopropane acid (XVIII) is found in the product, which consists entirely of a mixture of the normal and labile forms (XIX and XX) of β-methylglutaconic acid; showing that, whilst in the presence of this powerful reducing agent the three-carbon ring undergoes fission, nevertheless, the glutaconic system survives.



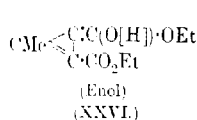
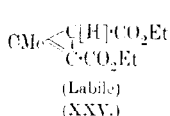
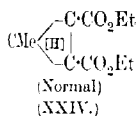
It has been noted on p. 328 that one of the most characteristic phenomena associated with mobile systems, such as the glutaconic acids, consists in their production by the easy elimination of groups from systems which thereby acquire the hydrogen atom necessary for tautomerism. The acid (XIV) offers a remarkable instance of the occurrence of this rather unusual type of reaction, since the bromo-substitution product (XXI), in which the bromine atom replaces the mobile hydrogen atom of the parent substance, is unstable in the presence of cold dilute alkalis, which reduce it quantitatively to the mobile acid (XIV) with the simultaneous production of alkaline hypobromite. From any point of view, other than that put forward in this paper, this reaction would be the more extraordinary by reason of the fact that the analogous saturated ring acids (XXII) and (XXIII) exhibit more than ordinary stability towards hydrolysing agents; for it has been shown (Ingold, T., 1921, 119, 314; 1922, 121, 2693) that these substances are only partly decomposed even after several weeks' continuous boiling with dilute alkalis. For example, we do not believe that any

allocation of plus and minus signs to the various atoms in the *cyclopropane* complex can be made the basis of a convincing explanation of such an extreme difference in the reactivity of similarly situated bromine atoms; on the other hand, the difference is entirely in accord with the general principles which have arisen during the study of the glutaconic acids and other mobile systems.



Although the *cyclopropene* acid (XIV) can be isolated in one form only, its ethyl ester exists in three well-defined modifications. Now it is evident that ordinary stereochemical theory cannot account for the existence of three forms of the unsaturated ester (XXV), because the methyl group and one carboxyl group lie in the plane of the ring; geometrical isomerism is therefore impossible, and the only reasonable alternative is to suppose that the difference between the esters is due to difference in the position of the mobile hydrogen atom, and that the esters are structural isomerides like the ketonic and enolic forms of ethyl acetoacetate. Actually a close examination of the esters proves this to be the case.

In the first place, it is to be noted that the general theory of glutaconic acid tautomerism indicates the existence of three isomeric esters of each acid, which may be respectively termed the normal ester, the labile ester, and the enol-ester. The normal, labile, and enol-esters of the cyclic glutaconic acid under consideration have respectively the formulae:



(Mobile hydrogen atom represented [H])

In the "normal" formula (XXIV), as in all formulae of the normal glutaconic type, the mobile hydrogen atom is placed at the centre of the three-carbon (glutaconic) system, in order to indicate that this three-carbon system represents the extent of what may loosely be described as the orbit of the hydrogen atom. Thus the "normal" formula is essentially a dynamic formula, whilst the "labile" formula, which obviously corresponds more closely with static structural ideas, contains the hydrogen atom on the α -carbon atom of the system, and therefore at the point of junction of the three-carbon system and the keto-enol system formed by the α -carbon atom and the adjacent carboethoxyl group. The hydrogen atom,

which is now only potentially mobile, has therefore two possible orbits : it may pass either into the three-carbon system to give the normal modification, or into the carbonyl system and thus give the enol-ester. Thus the normal ester can be converted into the enol-ester, and vice versa, only by way of the labile ester, which forms a halting-place in the two-stage migration of hydrogen from one triad system to the other.

Now in ordinary glutaconic esters, the normal, labile, and enol-esters appear to be progressively unstable in the order named. Thus glutaconic ester can be isolated in the normal form only, although the labile form has somewhat more than a momentary existence, as can be proved by generating it in the presence of a substance with which it can condense (Ingold and Thorpe, T., 1921, **119**, 492). In the case of β -methylglutaconic ester, both the normal and labile varieties can be isolated, although the labile form passes back into the normal on keeping for a few years at the ordinary temperature (Thorpe, T., 1919, **115**, 682).

In no case, however, has an enol-ester been isolated ; for although the yellow sodio-derivatives of the glutaconic esters are undoubtedly derived from these enolic forms, the free enol-esters, when liberated, even by weak acids such as carbon dioxide, pass into the labile esters (or into the normal esters if the labile esters are unstable) before isolation can be effected (Bland and Thorpe, T., 1912, **101**, 871, 1571).

In the case of the cyclopropene acid, however, the enol-ester can be isolated and preserved for several hours, or days, according to the temperature ; the labile ester can be preserved for several months, and the normal ester apparently indefinitely. Moreover, the properties of the three esters are completely in accord with the constitutions assigned to them.

In the first place, it is necessary to be sure that the isomerism is not physical. That it is not is shown, for example, by the fact that the esters differ from one another both physically and chemically in the liquid state and in solution ; that they can be separated from one another by physical or chemical means such as crystallisation, fractional distillation, or extraction with alkalis ; that interconversion in the dissolved state in the presence of a catalyst leads, not to a pure individual, but to an equilibrium mixture, which, after destruction of the catalyst, can be separated by the methods named.

The normal ethyl ester, m. p. $38-39^{\circ}$, b. p. $135^{\circ}/20$ mm., to which formula (XXIV) is assigned, undoubtedly has a structure closely analogous to that of the free acid, because although a mixture of both this and the labile and enol-esters is produced on esterifying the acid with alcohol and sulphuric acid in the ordinary

way, the ester, m. p. 38—39°, alone is formed when the silver salt of the acid is treated with ethyl iodide. Consequently this must be the normal ester, and its properties, for instance, its inability to yield a sodio-derivative without previous conversion into the labile form, its inability to give a coloured iron salt, and its stability towards additive reagents such as ethyl sodiocyanoacetate, are all completely analogous to the properties of all the normal esters of the glutaconic series.

The labile ester, b. p. 155°/20 mm., to which formula (XXV) is given, is easily distinguished from the normal ester by the fact that it quickly gives the yellow sodium salt of the enol ester on treatment with cold, dilute, alcoholic sodium ethoxide. The normal ester is unaffected by this treatment, and only on digestion with hot concentrated sodium ethoxide is converted into an equilibrated mixture, the composition of which is discussed in connexion with the general question of the interconversion of the three isomerides (p. 338). Again, in the course of time, cold concentrated aqueous alkalis convert the labile ester into alkali salts of the enol ester, but they have no action on the normal ester. On the other hand, the labile ester is sharply distinguished from the enol-ester, because the former is quite incapable of dissolving in dilute, cold alkalis and gives no immediate coloration with ferric chloride, although on keeping in contact with this reagent a colour slowly develops. The formation of iron salts from enol esters should be (and is) practically instantaneous (Knorr and Schubert, *Ber.*, 1911, **44**, 2772; Wislizenus, *Annalen*, 1896, **291**, 178), and the slow development of colour in the present instance affords a measure of the velocity of equilibration in the presence of a reagent for the enolic form.

Finally, the enol-ester (XXVI) is easily distinguished from both its isomerides by the fact that it is immediately soluble in cold, dilute sodium hydroxide, giving a yellow solution of its sodium derivative, and also by the immediate and intense coloration which it gives with ferric chloride. Moreover it is coloured, whilst both its isomerides are colourless (*vide infra*).

The conversion of the enol-ester (XXVI) into the labile ester (XXV) takes place with moderate rapidity, both in the liquid state and in solution, and in the latter case is catalytically accelerated by hydrogen ions. Thus the pure liquid enol-ester is almost completely converted into the labile isomeride on keeping at the ordinary temperature for twenty-four hours, or on distillation under reduced pressure. Again, if the deep orange solution of the sodium compound, prepared either from the labile ester and dilute sodium ethoxide, or from the enol-ester and dilute aqueous-alcoholic sodium hydroxide, is acidified with a weak acid, such as acetic acid,

it turns to an orange-brown shade of medium intensity, which then slowly fades, the solution becoming practically colourless in the course of half an hour: the solution now contains the labile ester (XXV). That the instantaneous colour change corresponds to the liberation of the coloured enol-ester (XXVI) from its salt is shown by the fact that the solution gives an immediate intense colour with ferric chloride, and that as the orange-brown colour fades (corresponding with the reversion of the enol-ester into the labile ester), so the intensity of the colour obtained with ferric chloride diminishes until, ultimately, the solution contains only the labile ester, which gives no immediate coloration. As in the case of many other keto-enol changes, the reaction is very sensitive to hydrogen-ion catalysis (Lapworth, T., 1904, 85, 30; Knorr, *Ber.*, 1911, 44, 1150), and if, for example, a drop of hydrochloric acid is added to the orange-brown solution of the enol-ester immediately after its liberation from the salt, the discharge of colour, indicating conversion into the labile ester, occupies only one or two minutes.

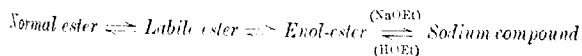
On general grounds, there can be no doubt that the retrograde change, that is, the conversion of the labile ester into the enol-ester, also takes place at the ordinary temperature and is catalysed by acids in the same way, and that the purest specimens of what we have hitherto termed the labile ester contain in reality a minute amount of the enol-ester in equilibrium with a large excess of the labile ester. However, the quantity of enol-ester must be very small, because it cannot definitely be detected by the ferric chloride test in specimens of the labile ester which have been kept long enough to ensure complete equilibration, although freshly prepared specimens show a weak, immediate reaction. Another point of interest is that the freshly distilled labile ester shows a weak, immediate reaction. It will be recalled that Knorr, Rothe, and Averbek (*Ber.*, 1911, 44, 1152) have recorded temporary increases in the enol content of freshly distilled ethyl acetoacetate. It has already been noted that the enol-ester itself cannot be distilled without reversion to the labile form, but if on general grounds we may assume that the enol-ester has the smaller vapour pressure, the temporary production of this substance by distillation of the labile ester falls well into line with the conversion of the normal ester into the labile ester described below.*

The interchanges between the normal and labile esters are considerably slower than those between the labile and enol esters. Thus the labile ester can be preserved at the ordinary temperature

* No doubt the same principle governs the conversion of normal glutamic anhydrides into the (presumably) less volatile hydroxy-anhydrides by distillation.

for days and even weeks, although an easily appreciable amount of conversion to the normal form takes place in the course of six months. Again, scarcely any interconversion takes place when either the normal or the labile ester is distilled in a water-pump vacuum, and, in fact, the two esters can be separated by fractional distillation, owing to the rather large difference in their boiling points. If, however, the normal ester is distilled at atmospheric pressure, the distillate consists of the pure labile ester. This result is easily interpreted, if it be recalled that the labile ester is considerably less volatile than the normal isomeride, and that at the higher temperature of a distillation under atmospheric pressure, equilibration will probably be extremely rapid. It follows that whatever may be the initial disturbance in the equilibrium due to vaporisation, the vapour will rapidly become equilibrated, and, on condensation, will deposit the least volatile constituent, so that, owing to the restoration in the vapour of the equilibrium thus disturbed, the condensate will consist solely of the labile isomeride, which, if the conditions are suitable, will fall into the cooled receiver too quickly for any appreciable reconversion to occur. This method of interconversion of tautomeric individuals has previously been employed in several well-known instances (for example, Meyer and Hopff, *Ber.*, 1921, 54, [B], 579). Doubtless conversion into the enol-ester, which is probably even less volatile, also takes place in the present case, under the conditions used, but since the labile-enol interchange is many hundred times faster than the normal-labile interchange, and in addition, overwhelmingly favours the labile ester, the cooling of the condensate is never rapid enough to lead to more than a slight (and temporary) enolisation of the labile ester obtained by distillation.

Owing to the slowness with which the normal-labile interconversion takes place at the ordinary temperature, our experiments on the reversibility of this reaction and on the nature of the equilibrium are still incomplete; but such evidence as exists at present appears to point to an equilibrium which favours the normal ester overwhelmingly. Sodium ethoxide, however, is a powerful catalyst, and leads rapidly to an equilibrium of the following type, in which the first two constituent equilibria represent the tautomerism of the glutaconic and keto-enol systems, respectively, and the third the reversible alcoholysis of the sodio-compound of the enol-ester:

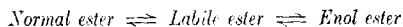


The formation of this sodium compound leads, of course, to the destruction of a considerable proportion of the normal ester which

would ordinarily be present in an equilibrium mixture of the normal, labile, and enol-esters. Actually, however, the equilibrium obtained by the use of one equivalent of sodium ethoxide still contains about 40 per cent. of the unchanged normal ester, traces only of the labile and enol esters, and about 60 per cent. of the sodium compound. The same equilibrium is obtained, no matter whether the normal or labile ester is employed originally, provided sufficient time is allowed (see table on p. 355). This reaction therefore forms another method by which the normal ester can be converted into the enol or the labile ester: for the sodium compound obtained from the equilibrium mixture can be converted at will either into the enol-ester by decomposing it with a deficit of hydrochloric acid, or into the labile ester by using a sufficient excess of hydrochloric acid to catalyse the isomeric change of the enol-ester first produced.

It may be added here, that in view of the catalytic activity of sodium ethoxide in promoting these tautomeric interchanges, the fact that the labile ester gives an almost immediate yellow colour with dilute alcoholic sodium ethoxide, whilst the coloured iron salt of the enol-ester is only slowly formed in the presence of ferric chloride, is quite easily understood.

An indication of the equilibrium ratios between the three esters in the absence of alkalis may be derived from the fact, that on esterification of the acid with alcohol and sulphuric acid the neutral product consists of 95 per cent. of the normal ester, 5 per cent. of the labile ester, and a qualitative trace of the enol-ester. That these figures substantially represent the true ratios for the system



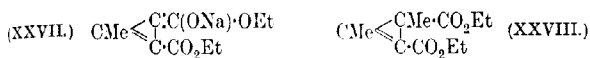
for the solvent ethyl alcohol and the temperature 100° , is proved by the fact that any one of the pure esters, when heated in ethyl alcohol containing a mineral acid such as sulphuric acid, is converted ultimately into a mixture of all three esters in the proportions named.

All three esters are converted into the same acid on hydrolysis with mineral acids, dilute alkalis, concentrated alkalis, and alkaline solutions containing casein.

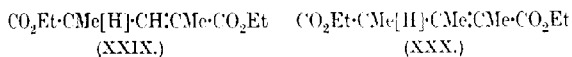
Corresponding with the three ethyl esters there are three methyl esters (normal, labile, and enol), which are prepared and converted one into the other exactly like the ethyl esters. The extreme similarity of corresponding methyl and ethyl esters, which relates not only to preparation, interconversion, and stability, but also to such details as fusibility, volatility, and velocity of interchange, will immediately be realised on referring to the descriptions given in the experimental portion of this paper, and it serves to confirm the

conclusions at which we have arrived in elucidating this somewhat complex doubly-tautomeric system.

It is a remarkable fact that the *cyclopropene* ester appears to be quite incapable of being alkylated. The sodium compound (XXVII) of the enol-ester is stable in the presence of ethyl alcohol and even water, as shown by the fact that the free enol-ester is immediately soluble in dilute sodium hydroxide; nevertheless, all attempts to replace the sodium by a non-ionisable group, such as an alkyl group, have proved unsuccessful. The probable reason for this is that a methyl derivative such as the ester (XXVIII) would contain no mobile hydrogen atom, and therefore would be incapable of assuming the glutaconic structure upon which, as it has already been shown, the stability of these *cyclopropene* compounds depends.



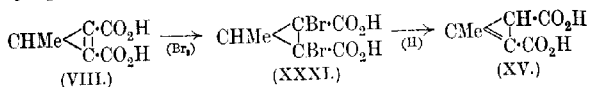
The methyl compound (XXVIII), like the bromo-compound (XXI), is therefore incapable of existence, at any rate in the presence of the reagents which might be expected to lead to its formation. In this respect, the *cyclopropene* ester is analogous to $\alpha\gamma$ -dimethylglutaconic ester (XXIX) and $\alpha\beta\gamma$ -trimethylglutaconic ester (XXX), neither of which can be further alkylated (Thorpe and Wood, T., 1913, 103, 1756), since neither ester contains an α - or γ -hydrogen atom which could become mobile, if the existing mobile hydrogen atom were replaced by an alkyl group.



This behaviour appears to be peculiar to glutaconic esters which contain but one potentially mobile hydrogen atom, and its occurrence in the case under consideration affords further evidence that this case falls strictly within the glutaconic conception.

It was stated on p. 331 that there is only one isolable form of the *cyclopropene* acid (m. p. 200°), that this has the "normal" structure (XIV), and that it adds on bromine by way of the labile form (XV), giving a dibromo-acid having formula (XVII). It is necessary now to examine more closely the evidence for these assertions because, owing to his incomplete appreciation of the glutaconic acid problem, Feist (*loc. cit.*) has been led to an erroneous conception of these substances. Thus he states that there are not one, but two isomeric *cyclopropene* acids (m. p.'s 200° and 189°), that the acid, m. p. 200°, has the symmetrical formula (VIII), and that this therefore gives a

dibromide of formula (XXXI) which on reduction gives the isomeric *cyclopropene* acid, m. p. 189°, formula (XV) :



We have carefully repeated the preparation of Feist's acids, m. p.'s 200° and 189°, and can definitely state that they are one and the same, that is, that the acid, m. p. 189°, is an impure form of the acid, m. p. 200°, which is the true melting point of the pure compound.

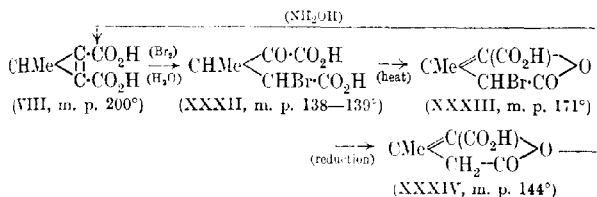
Feist mentions the following points of difference in the acids, m. p.'s 189° and 200° : (a) the solubilities of the two acids both in ether and chloroform are very different, (b) the crystalline forms of the calcium salts of the two acids are totally different, (c) one acid sublimes without decomposition, whilst the other does not, (d) the two acids differ by 11° in their melting points, which are not changed by recrystallisation.

As regards the first point, (a), a comparative examination of the solubilities of the two acids in different solvents has not revealed any essential difference between them. With regard to (b), Feist's own experiments show that in all respects, other than crystalline form, the two calcium salts are identical: thus both salts contain three molecules of water of crystallisation, two of which are lost at 120° and the third at about 200°. Since an examination of both calcium salts has shown that the crystals, which appear to conform to the trigonal system, are absolutely identical, the difference observed by Feist was probably due to a difference in size, or some other accidental circumstance. Regarding (c), the statement that the acid of higher m. p. sublimes, whilst the other does not, is readily explained by the fact that the latter is an impure form of the former, as it has been found that quite a small amount of impurity causes the acid to decompose rather than sublime. Finally with respect to the melting point, (d), it is clear that the reason why Feist was unable to remove the impurity from the lower-melting acid was because he employed water as solvent, from which it crystallises without loss of impurity. (Crystallisation from xylene at once raises the m. p. to 200°, and the product then sublimes readily and does not depress the m. p. of the original acid (200°).

* A substance having formula (XXXI) has been synthesised, and it has been found to yield the saturated *cyclopropane* acid (XV110), and not the *cyclopropene* acid, on reduction. The details of this experiment will shortly be published in another connexion.

It need scarcely be added that all mixtures of the specimens having m. p.'s 189° and 200° melt between these limits, and that both the pure and impure acids give the same ethyl ester, m. p. 38—39°, on esterification, and the same dibromide, m. p. 244°, on addition of bromine. It is plain, therefore, that Feist obtained only one *cyclopropene* acid, namely, the stable semi-aromatic substance of m. p. 200°.

It is, moreover, an easy matter to prove that this acid cannot have the structure assigned to it by Feist, because, as it can immediately be shown by simple qualitative tests, none of the derivatives which were prepared by Feist has properties corresponding with the formula assigned to it. Thus, by the action of bromine water, Feist obtained a bromo-acid, m. p. 138—139°, which on heating lost water, giving a bromo-lactone, m. p. 171° (Feist gives 168°); this on reduction gave a bromine-free lactone, m. p. 144° (Feist gives 141°), which on treatment with hydroxylamine passed back into the original *cyclopropene* acid, m. p. 200°. These reactions were interpreted as follows:



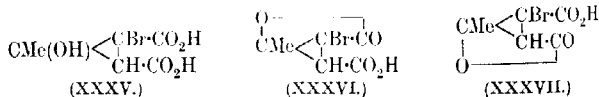
Now neither the bromo-lactone, m. p. 171°, nor the bromine-free lactone, m. p. 144°, both of which are formulated as unsaturated substances (XXXIII and XXXIV), decolorise cold alkaline permanganate, and indeed, they behave in every way as saturated substances. Again, the bromo-acid, m. p. 138—139°, which is represented as a keto-glutaric acid (XXXII), does not react with the usual reagents for ketones or α -ketonic acids (for example, semicarbazide and *o*-phenylenediamine). Moreover, it gives no coloration with ferric chloride, as α -ketoglutaric acid does (Ingold, T., 1921, 119, 328). Finally the conversion of a lactone of formula (XXXIV) into the *cyclopropene* acid (VIII) by the action of hydroxylamine seems too fantastic to be credible.

Further, it is shown in the present paper that the dibromo-acid, m. p. 244°, to which Feist assigns formula (XXXI), on mere heating in the dry state, in the absence of any reagent, gives the bromo-lactone, m. p. 171°, which would be impossible if this lactone had

Feist's formula (XXXIII). Even more difficult of interpretation would be the reconversion, also described in this paper, of the same lactone into the original dibromo-acid by the action of phosphorus pentachloride and bromine.

Thus there can be no doubt that the dibromo-additive product, m. p. 244°, has the unsymmetrical formula (XVII) and is formed by the addition of bromine to the labile form of the acid (XV). A second additive reaction of the labile modification is that which results in the formation of the bromo-hydroxy-acid (XXXV), m. p. 139°, by the addition of hypobromous acid. This formula (XXXV) is completely in agreement with the composition and properties of the substance, and therefore must replace the keto-glutaric formula (XXXII) assigned to it by Feist.

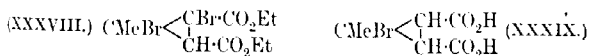
An examination of formula (XXXV) shows that the substance represented is both a β - and a γ -hydroxy-acid and might consequently lose water in either of two ways, giving an $\alpha\beta$ -unsaturated acid in one case and a γ -lactone in the other. If both types of dehydration occur, it is to be expected that dehydration resulting in the unsaturated acid would take place when lactone formation is prevented by the presence of alkalis. The $\alpha\beta$ -unsaturated acid to be expected is the bromo-unsaturated acid (XXI), which for reasons given on p. 332 would undergo spontaneous reduction to the original cyclopropene acid (m. p. 200°). The cyclopropene acid should therefore be the isolable product of the action of dilute alkalis, and this is actually the case, the change being complete after a few hours at the ordinary temperature or after a few minutes on boiling. The γ -lactone to be expected (it is also a β -lactone) has formula (XXXVI), which accounts for the fact that the lactone actually obtained, m. p. 171°, is saturated, and not unsaturated, as Feist represented it (formula XXXIII). The formation of the same bromo-lactone from the dibromo-acid (XVII) by the thermal elimination of hydrogen bromide, and its reconversion into the dibromo-acid by treatment with phosphorus pentachloride, bromine, and iron, are also reactions which are very simply accounted for by means of the formulae now assigned to these substances.



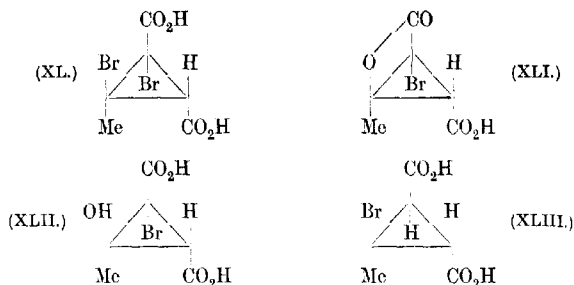
It will be noted that a second formula (XXXVII) expresses the formation and properties of the lactone, m. p. 171°, almost as well as the formula (XXXVI). Several circumstances, however,

indicate formula (XXXVI) as the more likely to be correct. For instance, it is well known that the *trans*-addition of bromine to unsaturated acids takes place as a rule much more easily than *cis*-addition. Assuming, therefore, that the bromine atoms in the dibromo-acid (XVII) are in the *trans*-position with respect to one another, and assuming also, on the grounds of the small tendency towards anhydride formation shown by the acid, that the carboxyl groups are also in the *trans*-position to one another, it follows that the lactone (XXXVI) is the only one which can be formed without change of configuration. This point will be rendered clearer by reference to the space formulæ (XL) and (XLI) given below.

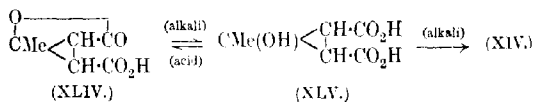
A number of other circumstances unite in indicating the correctness of the configurations assigned to these compounds. Thus the dibromo-ester (XXXVIII), which is readily prepared either by addition of bromine to the *cyclopropene* ester, or by esterification of the dibromo-acid, and which can be hydrolysed to the dibromo-acid, is smoothly converted by "molecular" potassium to the labile *cyclopropene* ester (XXV). This reaction certainly points to the bromine atoms being on opposite sides of the plane of the ring, since reactions of this type are usually very difficult to effect. Moreover, the space formula shows that although *trans*-elimination of bromine can take place, hydrogen bromide can be eliminated only from the *cis*-position; consequently it is not surprising to find that the dibromo-acid is stable towards cold dilute alkalis, and that the dibromo-ester is stable towards diethylaniline (Jones, T., 1905, **87**, 1064), although the bromo-hydroxy-acid (XXXV) loses the elements of water in contact with dilute alkalis, giving the bromo-unsaturated acid (XXI), which becomes spontaneously reduced to the original *cyclopropene* acid, m. p. 200°. This reaction corresponds with the *cis*-elimination of water (formula XLII). On the other hand, if the dibromo-acid is treated with sodium amalgam, the α -bromine atom becomes replaced by hydrogen, giving the monobromo-acid (XXXIX), which is now spontaneously converted by cold alkali into the *cyclopropene* acid, since *trans*-elimination of hydrogen bromide can now take place (formula XLIII).



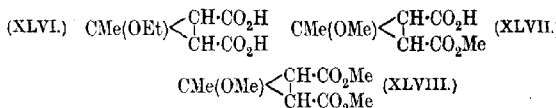
Thus the relative stabilities of the dibromo-acid and its more immediate derivatives are fully accounted for by the three-dimensional models of the formulæ which have been assigned to them.



Only one formula is possible for the reduced lactone, m. p. 144° (to which Feist assigned formula XXXIV), namely formula (XLIV), which also expresses its fully saturated character. As in the case of the bromo-lactone, the free hydroxy-acid (XLV) corresponding with the reduced lactone is both a β -hydroxy-acid and a γ -hydroxy-acid, and therefore might be expected to undergo dehydration in alkaline solution to give an $\alpha\beta$ -unsaturated acid, and in the absence of alkalis to give a γ -lactone, namely, the reduced lactone (XLIV). Actually, both these reactions occur. The free hydroxy-acid cannot be isolated, but its existence in solution is proved by the fact that on titrating a solution of the lactonic acid (XLIV) with ammonia, one equivalent is taken up in the cold and a second on warming. If, however, the attempt is made to isolate the acid by extraction with ether after acidification, it undergoes dehydration after the manner of a γ -hydroxy-acid, and only the lactone (XLIV) is obtained. On the other hand, if the solution is left for some hours in contact with a sufficient excess of alkali to prevent lactone formation, dehydration of the other type takes place and the original *cyclopropene* acid is obtained :

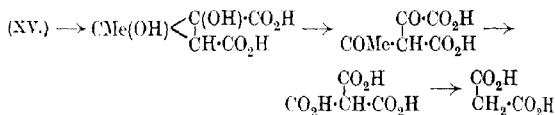


This is the explanation of Feist's supposed conversion of the lactone (XXXIV) into the original *cyclopropene* acid by means of hydroxylamine. We have confirmed Feist's observation that the lactone, m. p. 144°, yields the *cyclopropene* acid, m. p. 200°, when left in contact with hydroxylamine hydrochloride and excess of sodium carbonate; but the real reagent is the excess of alkali, and Feist overlooked the fact that the reaction takes place just as well if the hydroxylamine hydrochloride is omitted.

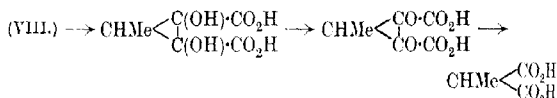


The position of the alkoxy-group in these compounds is proved by the fact that they yield β -methylglutaconic acid on reduction by hydriodic acid, the reaction taking place by way of the *cyclopropene* acid.

Further evidence of the existence of the labile acid is obtained on oxidation in alkaline solution by permanganate, when seven atoms of oxygen are taken up and malonic acid is produced :



It may be noted in passing that an acid of the formula (VIII), assigned by Feist to the *cyclopropene* acid, m. p. 200°, should on oxidation yield, not malonic acid, but methylmalonic acid, which, actually, is not produced :



It is plain, therefore, that in this *cyclopropene* acid, as well as in all mobile glutaconic acids, we meet with certain of the properties of the labile modification, in addition to the semi-aromatic character manifested by the remarkable stability discussed in the earlier pages of this paper. On the whole, the acid may be said to be a typical mobile glutaconic acid, but in how far cyclic three-carbon tautomeric systems will in general be found to conform to the conception of the semi-aromatic state cannot be decided in the absence of additional experimental evidence such as we hope shortly to provide.

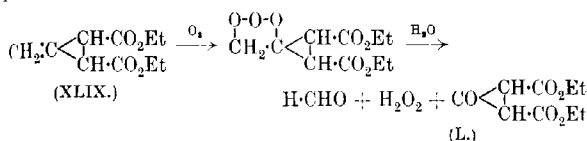
Addendum.*

When this paper was read before the Society, the criticism was raised that no definite proof had been furnished showing that one of the two forms of the ester (XXIV) which gave no colour with ferric chloride had not a structure represented by the extra-cyclic double-bonded formula (XLIX) which, it will be noted, is the only other possible form unless the hypothesis brought forward in this

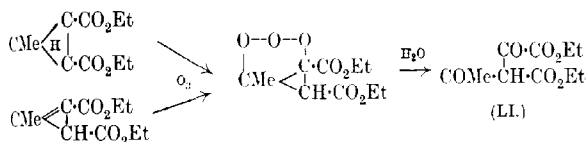
* [Received, January 12th, 1923.]

paper is accepted. The criticism seemed to us so apposite that we decided to meet it before publication by investigating the action of ozone on the normal and labile esters (XXIV and XXV), which should, if the structures assigned to them are correct, react in the form (XXV).

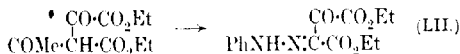
The products to be expected from the fission by water of the ozonide of an ester of formula (XLIX) are the *cyclopropanone* ester (L) or its degradation products together with formaldehyde and possibly formic acid :



If, however, either or both of the esters have the formulæ assigned to them by us, they would yield on similar treatment only one fission product, namely, the ketonic ester (LI) :



Actually no formaldehyde could be detected on hydrolysing the ozonides of either the normal or labile ester, whilst the sole product was ethyl acetyloxaloacetate (LI) (Nef, *Annalen*, 1893, **276**, 221), which was identified by its boiling point and by analysis and by converting it into the crystalline β -ethyl diketosuccinate phenylhydrazone (LII) through the agency of benzenediazonium chloride (Rabischong, *Bull. Soc. chim.*, 1904, [iii], **31**, 93), a specimen of the phenylhydrazone being synthesized for direct comparison :



EXPERIMENTAL.

(A)—3-Methyl- Δ^2 -cyclopropene-1 : 2-dicarboxylic Acid.

The *cyclopropene* acid required for this investigation was prepared by a method essentially the same as that described in the literature, namely, the following series of reactions : ethyl acetoacetate \longrightarrow ethyl isodehydracetate \longrightarrow ethyl bromoisodehydracetate \longrightarrow methylcyclopropenedicarboxylic acid (Duisberg, *Annalen*, 1882,

213, 133; *Ber.*, 1882, 15, 1387; Hantzsch, *Annalen*, 1883, 222, 1; Polonowska, *Ber.*, 1886, 19, 2402; Anschütz, Bendix, and Kerp, *Annalen*, 1890, 259, 148; Genvresse, *Ann. Chim. Phys.*, 1891, [vi], 24, 88; Hantzsch, *Ber.*, 1892, 25, 1310; Feist, *Ber.*, 1893, 26, 767; *Annalen*, 1906, 345, 60). However, in view of the fact that a large amount of this acid was required, the details of each stage in the above series of reactions were carefully studied, and the process so considerably improved that the preparation of large quantities is now an easy matter, 1 kilo. being obtainable from only 6 kilos. of ethyl acetoacetate.

Ethyl isodehydracetate.—Ethyl acetoacetate (1500 grams) was cooled in an efficient freezing mixture and treated for eight hours with a rapid stream of dry hydrogen chloride. The liquid was kept in the dark and protected from moisture for a week, and then again cooled and saturated with hydrogen chloride as before. At the end of a further week, the liquid was shaken with 3 litres of water and then with 750 c.c. of a *N*-solution of sodium carbonate. The aqueous washings were evaporated to small bulk and the residue dried in an evacuated desiccator over potassium hydroxide; the sodium carbonate washings were acidified with hydrochloric acid and extracted with ether. This extract, together with the residue from the aqueous washings and 500 c.c. of ether, was added to the main bulk of the oil, which was then dried with anhydrous sodium sulphate, and after removing the ether, distilled under reduced pressure, the fraction, b. p. 160–190°/20 mm., being collected for bromination (see below). The yield was 700 grams, that is, 63 per cent. of the theoretical.

Ethyl Bromoisodehydracetate.—Ethyl isodehydracetate (500 grams), dissolved in one litre of chloroform, was cooled in ice, and 150 c.c. of dry bromine were added from a dropping funnel, the flask being shaken occasionally. After leaving over-night, the hydrobromic acid was removed on the steam-bath, and the cooled solution diluted with 1 litre of ether, and washed with water and sodium carbonate solution. After drying with calcium chloride, the solvents were distilled off, and the residue, which solidified to a hard cake, crystallised from a small amount of 95 per cent. alcohol, and thus obtained as large, pale yellow, monoclinic crystals, m. p. 87°. The yield was 600 grams, that is, 83 per cent. of the theoretical.

3-Methyl- Δ^2 -cyclopropene-1:2-dicarboxylic Acid (XIV).—A 28 per cent. solution of potassium hydroxide (275 c.c.) was boiled in a 1500 c.c. flask and 50 grams of fused ethyl bromoisodehydracetate were rapidly added, the flask being inclined at an angle of 40° to prevent loss during the violent evolution of alcohol which occurred

about one minute after the addition. Boiling was continued for thirty minutes. When cool, the solution was cautiously neutralised with a mixture of 45 c.c. of sulphuric acid and 45 c.c. of water, and the acid solution, together with precipitated potassium sulphate, repeatedly extracted with ether, the aqueous solution being finally evaporated almost to dryness and again extracted. The dried ethereal extracts on evaporation left a semi-solid residue, which was freed from alcohol and acetic acid in an evacuated desiccator containing potassium hydroxide. The darkly coloured solid was dissolved in water and the solution boiled with 1 gram of freshly ignited animal charcoal for five hours, after which the liquid was filtered while hot, and evaporated to dryness. The crude acid, after being dried on porous plates, was either recrystallised from ethyl acetate, or if required for the preparation of its esters, directly esterified. The yield was 15.5 grams, that is, 60 per cent. of the theoretical.

The acid may be obtained in a pure condition by crystallisation from xylene, from which it separates in small needles; or it may be sublimed, and thus obtained in long needles. The melting point is 200° in all cases, and there is evolution of gas at 220° . Specimens of the acid from which the last traces of certain impurities have not been removed decompose at the melting point.

The individuality of this acid has been discussed on p. 339 *et seq.*, and nothing further need be added here. Its formation by hydrolysis of its normal, labile, and enol esters, by reduction of its dibromo-additive product, by the action of alkalis on its hypobromous acid additive product, and by the action of alkalis on the lactone of 3-hydroxy-3-methylcyclopropane-1:2-dicarboxylic acid is described on pp. 352—359. Contrary to the statement of Feist, the acid appears to have no tendency to yield an anhydride when boiled with acetyl chloride or acetic anhydride. Indeed it would not be expected that an acid which sublimes without decomposition would form an anhydride easily. There is, however, evidence of the formation of a hydroxy-anhydride when the acid is heated at 220° in closed tubes with acetic anhydride.

The acid (15 grams) was treated with 150 c.c. of acetic anhydride at 220° for five hours. On removing the excess of acetic anhydride by distillation, and extracting the residue with benzene, a liquid was obtained which boiled at $185-190^{\circ}$ 20 mm., and had all the properties of the expected hydroxy-anhydride. Thus it gave an alkali salt, and a coloured iron salt, and yielded the original acid on rehydration. The specimen was insufficient for redistillation and could not be completely purified, but we hope in the near future to effect an improvement on this wasteful method of preparation, and then to

study the process of rehydration (especially in the presence of casein) in greater detail.

(B)—*The Normal, Labile, and Enol Esters of 3-Methyl- Δ^2 -cyclopropene-1 : 2-dicarboxylic Acid.*

The Three Ethyl Esters : Formation by Direct Esterification.—When the acid, m. p. 200° , was esterified with ethyl alcohol and sulphuric acid, the product consisted of a mixture of the three isomeric forms of the diethyl ester. Most of the normal ester, which was present to the extent of 95 per cent. of the whole, crystallised at the ordinary temperature, and the remainder was deposited practically completely when the liquid residue was cooled to -40° . It was collected on a well-cooled filter, and drained on porous porcelain until it no longer imparted a yellow colour to 40 per cent. aqueous potassium hydroxide at 40° (proof of the absence of the labile and enol-esters), and had the correct melting point ($38-39^\circ$).

The filtrate from the normal ester was dissolved in ether and extracted at the ordinary temperature with 10 per cent. potassium hydroxide to remove the enol-ester. On drying and evaporating the ether, a residue was obtained which consisted of the pure labile modification, since it boiled constantly at $155^\circ/20$ mm. (see below), and gave an immediate colour with 40 per cent. potassium hydroxide at 40° , but gave no immediate colour with cold 10 per cent. potassium hydroxide or with ferric chloride. The amount obtained was 4–5 per cent. of the total esters.

The alkaline extract was cautiously neutralised, and the precipitated ester extracted with ether. The residue which was left on drying and evaporating the ether consisted of a small qualitative trace of the enol-ester. It gave an immediate, intense red colour with ferric chloride, and was immediately, and completely soluble in cold 10 per cent. potassium hydroxide.

Normal Ethyl 3-Methyl- Δ^2 -cyclopropene-1 : 2-dicarboxylate (XXIV).—This ester may be prepared in several ways :

(1) By direct esterification of the acid with ethyl alcohol, which gives the normal ester to the extent of about 95 per cent. (Jones, T., 1905, 87, 1064).

(2) By digesting the silver salt of the acid with ethyl iodide, which gives the normal ethyl ester only.

(3) By heating either the labile or enol ester in ethyl alcoholic solution containing sulphuric acid.

(4) By keeping either the labile or enol ester at the ordinary temperatures for one to two years, when the normal ester only is obtained.

(5) By treating either the labile or enol ester with sodium ethoxide for two days at 60°; conversion into the normal ester then takes place to the extent of 40 per cent.

Method (1) is described on p. 350, method (4) on p. 354, and method (5) on p. 354; the details of methods (2) and (3) are as follows. The silver salt, prepared from a neutral solution of the ammonium salt, was washed and dried (it is not affected by daylight), and then shaken with an ethereal solution of the theoretical quantity of ethyl iodide. On filtering and evaporating the solution, the pure normal ester was obtained in large, rhombic crystals, which melted at 38—39°, giving a colourless liquid which boiled constantly at 135°/20 mm., without decomposition or conversion into its isomerides.

The normal ester crystallises very slowly from specimens of the labile ester which have been seeded with the normal ester at 0° and then preserved at the ordinary temperature in the absence of solvents. It is estimated that about two years would be required for the completion of the interchange, although a specimen has not yet been preserved long enough to verify this. Since the enol-ester passes into the labile ester in the course of one day at the ordinary temperature, similar results are obtained when the labile ester is replaced by the enol-ester in the above experiment.

The normal ester may be separated from mixtures with its labile isomeride in three ways:

(1) By freezing out at -40°. This is described on p. 350.

(2) By fractional distillation under reduced pressure. The labile ester boils at a temperature 20° higher than the boiling point of the normal ester at 20 mm., and therefore the two can be separated almost quantitatively by distillation, if reasonably large quantities are employed.

(3) By means of dilute sodium ethoxide. Cold dilute sodium ethoxide does not convert the normal ester into its isomerides at any appreciable speed, but it at once reacts with the labile ester, yielding the sodium compound of the enol-ester. If the product is now poured into water and extracted with ether, the normal ester is recovered in the pure condition, whilst the labile ester can be obtained by adding to the aqueous solution an excess of mineral acid, which quickly converts the liberated enol-ester back into the labile form. This separation is quantitative.

The normal ester is separated quantitatively from mixtures with the enol-ester by shaking with 10 per cent. aqueous potassium hydroxide, which dissolves the latter.

The normal ester is converted into the labile ester by distillation under atmospheric pressure (p. 352). It is converted to the extent

of about 60 per cent. by concentrated alcoholic sodium ethoxide at 60° into the sodium salt of the enol-ester, from which either the free enol-ester or the labile ester can be obtained at will (p. 354). Finally, the normal ester is converted, to the extent of 5 per cent., into the labile ester by heating with alcohol and sulphuric acid (p. 354).

The ester yields the parent cyclopropene acid on hydrolysis either with hydrochloric acid or with dilute or concentrated potassium hydroxide. It takes up bromine fairly readily, and discharges the colour from an alkaline solution of permanganate.

Labile Ethyl 3-Methyl- Δ^2 -cyclopropene-1:2-dicarboxylate (XXV).

—This modification may be obtained in four ways :

(1) By esterification of the acid, which yields the labile ester to the extent of 5 per cent. (p. 350).

(2) From the normal ester by heating with alcohol and sulphuric acid (p. 354).

(3) From the normal ester by distillation under atmospheric pressure.

(4) From the enol-ester by keeping, by acid catalysis at the ordinary temperature, or by heating.

The distillation of the normal ester at 236°/758 mm. constitutes the best method of obtaining the labile ester in quantity, although the yield is reduced by about 40 per cent., by reason of the fact that a certain amount of the material is simultaneously converted into a non-volatile polymeride, which has not yet been investigated. The distillate, when freshly collected, contains a more or less considerable quantity of the enol-ester, as may be shown by the fact that it gives an immediate colour with ferric chloride, and also by the fact that a portion of it is soluble in cold 10 per cent. aqueous potassium hydroxide. The pure labile ester may be obtained either by extracting the enol-ester with dilute alkali, or by merely keeping the distillate for twenty-four hours, by which time the enol-ester has reverted practically completely to the labile ester.

The enol-ester (p. 353) passes into the labile ester in the course of one day at the ordinary temperature in the absence of deliberately added catalysts, in about half an hour at the ordinary temperature in the presence of acetic acid, and in about two minutes in the presence of hydrochloric acid. At higher temperatures, these changes are correspondingly more rapid. On distillation at 155°/20 mm., the enol-ester yields a mixture of the labile ester and some unchanged enol-ester, the quantity depending on the conditions of the condensation.

The separation of the labile ester from mixtures with the normal ester has been described on p. 351. It is separated from the enol-

ester by extracting the latter with dilute alkalis, the process being quantitative, if cold 10 per cent. potassium hydroxide is employed.

The labile ester may be converted into the normal ester by keeping at the ordinary temperature for one to two years (p. 351), to the extent of 40 per cent., by heating with concentrated alcoholic sodium ethoxide (p. 354), and to the extent of 95 per cent. by heating with ethyl alcohol and sulphuric acid. It may be quantitatively converted into the enol-ester by way of the sodio-derivative, which is produced in the presence of cold dilute alcoholic sodium ethoxide, and partly converted into the enol-ester by distillation under 20 mm. pressure. The quantity of enol-ester formed in this way depends on the rapidity of condensation, and on the completeness with which catalysts are eliminated, and experiments are now in progress by means of which it is hoped so far to improve the technique of the operation as to obtain complete conversions by "aseptic" distillation.

The labile ester becomes very viscous at -40° , but shows no tendency to crystallise; it boils, under "non-aseptic" conditions, constantly at 155° /20 mm. It immediately decolorises cold alkaline permanganate, and rapidly absorbs bromine. On hydrolysis with hydrochloric acid, dilute or concentrated potassium hydroxide, or potassium hydroxide in the presence of casein, it gives the normal acid, m. p. 200° (Found: C = 60.5; H = 7.1. $C_{10}H_{14}O_4$ requires C = 60.6; H = 7.1 per cent.).

Endic Ethyl 3-Methyl- Δ^2 -cyclopropene-1:2-dicarboxylate (XXVI).—This ester may be prepared in the following ways:

- (1) In small amount, by direct esterification of the acid (p. 350).
- (2) In small amount, by heating either of the other esters with alcohol and sulphuric acid (p. 354).
- (3) In small amount, by distillation of the normal ester under atmospheric pressure (p. 352), or by distillation of the labile ester under reduced pressure (p. 353), the separation being effected with the aid of dilute alkalis as in (1).
- (4) To the extent of about 60 per cent. by the action of hot concentrated sodium ethoxide on the normal ester (p. 354).
- (5) Quantitatively, by the action of cold dilute sodium ethoxide on the labile ester.

When the labile ester was added to the theoretical quantity of cold dilute alcoholic sodium ethoxide, an intense orange colour was immediately developed and a considerable amount of heat was evolved. The solution was kept for ten minutes, poured into water, and cautiously treated with a slight deficit of dilute hydrochloric acid. The precipitated ester was extracted with pure ether, washed with dilute sodium hydrogen carbonate and with water, and then

recovered by drying and evaporating the ether. It was completely soluble in 10 per cent. aqueous potassium hydroxide and gave an immediate, intense crimson colour with ferric chloride.

This ester can be quantitatively separated from mixtures with the normal and labile esters by extraction with cold 10 per cent. potassium hydroxide. The various ways in which the enol-ester can be converted into the labile ester are enumerated on p. 352, and its transformation by way of the labile ester into the normal ester by keeping, and by the action of hot concentrated sodium ethoxide, is noted on pp. 351 and 354 (below).

The enol-ester rapidly decolorises alkaline permanganate and bromine. On hydrolysis with alkalis, either with or without the addition of casein, it yields the normal acid, m. p. 200° . The sodium and potassium derivatives are obtained by interaction of the labile or enol ester and sodium or potassium ethoxide, but they are resinous and cannot be crystallised. They show no tendency to react with ethyl sodiocyanoacetate and do not give rise to alkyl derivatives when boiled in alcoholic solution with alkyl iodides.

Equilibration of the Three Esters in Alcoholic Solution.—Each of the three isomeric esters, when heated at 100° in ethyl alcohol containing sulphuric acid, the conditions being similar to those used in esterifying the acid (p. 350), was converted into a mixture of the normal, labile and enol-esters, which were separated by the methods previously described. The proportions were the same as in the esterification of the acid.

Equilibration of the Esters in the Presence of Sodium Ethoxide.—A series of experiments, made with the object of examining the nature and speed of adjustment of the equilibrium which is established when any one of the three esters is treated with an equivalent of alcoholic sodium ethoxide, has led to the conclusion that after a period of two days at 60° equilibration is complete, and that in this state the two intermediate members of the series normal ester \rightleftharpoons labile ester \rightleftharpoons enol-ester \rightleftharpoons sodium derivative are almost entirely absent, the mixture consisting of about 40 per cent. of the normal ester and 60 per cent. of the sodium compound of the enol-ester. A small amount of the material, however, undergoes a side reaction leading to the ethoxy-acid mentioned below (section F).

In each of the experiments, the results of which are shown in the following table, 10 grams of a pure ester were treated with one equivalent of alcoholic sodium ethoxide under the conditions named, and the product separated by pouring into water, extracting the normal ester with ether, and then decomposing the sodium compound by neutralising the aqueous liquid with hydrochloric acid. The enol-ester was then extracted and separated from the

small amount of ethoxy-acid by means of dilute sodium hydrogen carbonate. The total amount of recovered material was usually 9 grams or a little less.

Conditions.	From normal ester.			From labile or enol-ester.		
	Normal ester. (gms.)	Enol-ester. (gms.)	Ethoxy-acid. (gms.)	Normal ester. (gms.)	Enol-ester. (gms.)	Ethoxy-acid. (gms.)
10 minutes at 25° ...	9	0	0.0	0	9	0.0
1 hour at 60°	6	2	0.2	1	8	0.0
48 hours at 60°	3	5	0.6	3	5	0.6

The Three Methyl Esters.—The cyclopropene acid forms three isomeric methyl esters, which are precisely analogous to the three ethyl esters just described.

Normal Methyl 3-Methyl- Δ^2 -cyclopropene-1 : 2-dicarboxylate.—This ester can be obtained by methods analogous to the first four of the five methods given on p. 351, for the preparation of the normal ethyl ester. It can be separated from the labile and enol methyl esters by the methods used for the separation of the normal ethyl ester from its isomerides. It crystallises in needles, m. p. 33–34°, boils at 122°/20 mm., and at 782 mm. distils with very little polymerisation, giving the pure labile ester. It reacts with hot methyl alcoholic sodium methoxide, giving the methoxy-esters described in section G, and in other respects, for instance towards permanganate, bromine, and hydrolysing agents, behaves similarly to the normal ethyl ester.

Labile Methyl 3-Methyl- Δ^2 -cyclopropene-1 : 2-dicarboxylate.—This ester is prepared, and is separated from, and converted into its isomerides exactly like the labile ester in the ethyl series, excepting in regards its reaction with sodium methoxide, which is described in section G. Under "non-aseptic" conditions it boils constantly at 135°/20 mm.

Enol Methyl 3-Methyl- Δ^2 -cyclopropene-1 : 2-dicarboxylate.—This is obtained by methods analogous to methods (1) (2) (3) and (5) (p. 353) for the preparation of the enol ethyl ester, to which it is similar in all respects, excepting the reactions described in section G.

(C) *The Action of Ozone on the Normal and Labile Esters of 3-Methyl- Δ^2 -cyclopropene-1 : 2-dicarboxylic Acid. Ethyl Acetyloxaloacetate (Li).*

The Normal Ester.—The solid ester (5 grams), dissolved in 10 c.c. of chloroform, was subjected to a strong current of ozone over a period of six hours. The solvent on evaporation left a colourless oil (yield theoretical) (Found : C = 49.6; H = 6.3. $C_{10}H_{14}O_7$ requires C = 48.8; H = 5.7 per cent.), which was warmed for two hours with

50 c.c. of water in a flask fitted with a ground-in condenser at the end of which was fitted a bubbler containing Schiff's reagent to detect any formaldehyde which might be formed. However, the reagent developed no colour nor, on testing the aqueous solution, could the presence of formaldehyde be detected.

The solution was extracted with ether and the pale yellow oil so obtained was distilled (yield 3 grams) and identified as ethyl acetyl-oxaloacetate by analysis (Found: C = 51.8; H = 6.2. Calc., C = 52.1; H = 6.2 per cent.), by its ferric chloride reaction, its solubility in aqueous alkali, and by treatment with an acid solution of benzenediazonium chloride (Rabischong, *Bull. Soc. chim.*, 1904, [iii], 31, 93), which gave β -ethyl diketosuccinate phenyl-hydrazone (LII) as yellowish-red needles, m. p. 72–73°, which were identified by direct comparison and the method of mixed melting points with an authentic specimen prepared from ethyl oxaloacetate (*ibid.*, p. 78).

The Labile Ester.—Experiments were carried out with the labile ester under conditions identical with those employed with the normal ester, excepting that it was found necessary to pass ozone for a longer period. No formaldehyde could be detected and the products obtained were identical with those given above.

(D) *Reduction of 3-Methyl- Δ^2 -cyclopropene-1:2-dicarboxylic Acid: Formation of Normal and Labile β -Methylglutaconic Acids.*

(i) *Action of Sodium Amalgam.*—Many attempts were made to reduce the cyclopropene acid by means of 4 per cent. sodium amalgam, both at the ordinary temperature and in boiling solution, under different conditions of alkalinity or acidity. In no case was any evidence of reduction obtained, the acid being invariably recovered unchanged.

(ii) *Action of Hydriodic Acid.* The cyclopropene acid can be reduced by hydriodic acid, but only under energetic conditions, as the following typical experiments show.

(a) The cyclopropene acid (2 grams) was boiled under reflux with 10 c.c. of hydriodic acid (*d* 1.7) for one hour, and the product diluted with water and extracted with ether. The extract was decolorised by means of potassium hydrogen sulphite solution, dried, and evaporated, when the cyclopropene acid was recovered unchanged.

(b) The preceding experiment was repeated with the modification that 2 grams of red phosphorus were added before boiling. The result was the same.

(c) The conditions of experiment (a) were reproduced, excepting that the heating was continued for five hours. The product, isolated in the same manner and purified by crystallisation from

xylene, melted at 115° , and did not depress the melting point of an authentic specimen of labile β -methylglutaconic acid, with which direct comparison showed its identity (Found : C = 50.1; H = 5.7. Calc., C = 50.0; H = 5.6 per cent.).

(d) The conditions of experiment (b) were reproduced, excepting that the mixture was heated at 180° in a sealed tube for six hours. The reduction product, isolated as before and fractionally crystallised from xylene, yielded two acids. That present in larger amount melted at 149° and had all the properties of normal β -methylglutaconic acid, with which it was identified by direct comparison. The other acid melted at 115° and was identified as labile β -methylglutaconic acid. No trace of 3-methylcyclopropane-1 : 2-dicarboxylic acid, or of glutaric acid, could be isolated.

(E) *Addition of Bromine to the cycloPropane Acid and its Esters.*

2 : 3-Dibromo-3-methylcyclopropane-1 : 2-dicarboxylic Acid (XVII).—It is unnecessary to heat the cyclopropene acid with excess of bromine in a sealed tube in order to obtain this substance (Feist, *loc. cit.*). The acid (5 grams) was dissolved in 300 c.c. of dry ether containing 2.5 c.c. of dry bromine, and the solution, after keeping over-night in a closed flask, was shaken with potassium hydrogen sulphite, dried, and evaporated. The residue consisted of the pure libromo-acid, which crystallised from xylene in needles, and from water in plates, m. p. 244° (decomp.). The acid may also be prepared (p. 358) from its ethyl ester, and from the bromo-lactone mentioned below.

The acid could not be converted into an anhydride by boiling with acetyl chloride, which indicates that the carboxyl groups are in the *trans*-position with respect to each other. It could not be converted into the anhydride of the *cis*-modification, because on sublimation, and on heating in a sealed tube with acetic anhydride, it lost hydrogen bromide, yielding the lactone of 2-bromo-3-hydroxy-3-methylcyclopropane-1 : 2-dicarboxylic acid (p. 358). The acid is stable towards boiling hydrochloric acid or cold alkali hydroxides, but boiling alkali hydroxides convert it into a syrupy product, from which no pure substance has up to the present been obtained.

Reduction of the Dibromo-acid.—This was carried out using sodium amalgam as described by Feist (*loc. cit.*). The product melted at 189 — 190° , both in the crude state and after crystallisation from water, but two crystallisations from xylene brought the m. p. to 200° . A direct comparison on the lines indicated on p. 340 showed that the substance was 3-methylcyclopropene-1 : 2-dicarboxylic acid, and this conclusion was confirmed by a microscopic

examination of the calcium salt and by the preparation of the normal ethyl ester and the dibromo-acid.

Ethyl 2 : 3 - Dibromo - 3 - methylcyclopropane - 1 : 2 - dicarboxylate (XXXVIII).—This ester was prepared by the action of bromine on the cyclopropene ester as described by Jones (*loc. cit.*), and also by directly esterifying the dibromo-acid with ethyl alcohol and sulphuric acid. It was obtained as a colourless oil, b. p. $170^{\circ}/5$ mm., the yield being 80 per cent. of the theoretical. The decomposition observed by Jones, who distilled under 30 mm., does not occur at pressures below 15 mm.

On hydrolysis by boiling with hydrochloric acid, this ester is converted into the dibromo-acid, m. p. 244° .

Reduction of the Dibromo-ester.—Seven grams of the ester were gradually added to a suspension of 1.6 grams of finely divided potassium in xylene, the mixture being cooled meanwhile, as much heat was evolved. After filtering, the solution was distilled under reduced pressure, when an almost quantitative yield of the labile modification of the cyclopropene ethyl ester was obtained.

(F) *Addition of Hypobromous Acid to the cycloPropene Acid.*

2-Bromo-3-hydroxy-3-methylcyclopropane-1 : 2-dicarboxylic Acid (XXXV).—This acid was prepared, following the directions given by Feist (*loc. cit.*), by the action of bromine water on the cyclopropene acid. After crystallisation from ether, it melted at 138 – 139° . It does not give a colour with ferric chloride and does not react with semicarbazide acetate or *o*-phenylenediamine. On sublimation, or evaporation in acid solution, it is converted into the lactone mentioned below, and on treatment with alkalis undergoes spontaneous reduction to the cyclopropene acid, m. p. 200° .

Spontaneous Reduction in Alkaline Solution.—(a) Five grams of the bromo-hydroxy-acid were dissolved in 200 c.c. of 10 per cent. aqueous potassium hydroxide, and the solution was left at the ordinary temperature until the next day, when it was acidified with hydrochloric acid and extracted with ether. The acid isolated in this way melted at 200° after crystallisation from xylene, and was identified as the original cyclopropene acid.

(b) The same result was obtained when the solution in 10 per cent. potassium hydroxide was boiled one hour and then acidified and extracted with ether.

In either experiment, the bromo-hydroxy-acid may be replaced by its lactone (below), without altering the result.

Lactonic Acid of 2-Bromo-3-hydroxy-3-methylcyclopropane-1 : 2-dicarboxylic Acid (XXXVI).—This substance may be prepared in three ways :

(a) By subliming the free hydroxy-acid (Feist, *loc. cit.*), or by evaporating it in acid solution.

(b) By heating the dibromo-acid, m. p. 244° , when hydrogen bromide is eliminated, and a sublimate of the bromo-lactone is obtained.

(c) By prolonged boiling of the dibromo-acid with water and subsequent evaporation.

It crystallises from xylene in short needles, m. p. 171° , and sublimes in glistening plates. It does not decolorise alkaline permanganate, but alkalis convert it into the hydroxy-bromo-acid and thence into the cyclopropene acid (above), and sodium amalgam reduces it to the lactone having formula (XLIV). Phosphorus pentachloride and bromine convert it into the chloride of the dibromo-acid, m. p. 244° .

Bromination by Phosphorus Pentachloride and Bromine.—The lactonic acid (2.5 grams) was heated with the same weight of phosphorus pentachloride until the reaction was finished, when a small amount of iron and 2 c.c. of bromine were added and the mixture was gently heated on the steam-bath for sixteen hours. The excess of bromine was then removed in a current of air and the residue poured into ethyl alcohol. The neutral esters were isolated by adding water and extracting with ether in the usual way, and hydrolysed by boiling with 20 per cent. hydrochloric acid, from which the dibromo-acid, m. p. 244° , crystallised on cooling.

Lactonic Acid of 3-Hydroxy-3-methylcyclopropane-1:2-dicarboxylic Acid (XLIV).—This substance, which has been described by Feist (*loc. cit.*), is best obtained by dissolving the bromo-lactonic acid in water and gradually adding an excess of 4 per cent. sodium amalgam while a rapid stream of carbon dioxide is passed and the temperature maintained at $50-60^{\circ}$. After cooling, the solution is acidified and extracted with a large amount of ether. The lactonic acid crystallises from xylene in minute needles, m. p. 144° (Found: C = 50.7; H = 4.5. Calc., C = 50.7; H = 4.2 per cent.), and sublimes with light decomposition.

The free hydroxy-acid corresponding with this lactone cannot be isolated, although its salts are obtained by the action of alkalis on the lactonic acid; the free hydroxy-acid is, however, very easily lehydrated by excess of alkalis, giving the cyclopropene acid (below). Solutions of the lactonic acid in cold sodium hydrogen carbonate do not decolorise permanganate.

Conversion into the cyclopropene Acid.—The lactonic acid (0.5 gram), dissolved in 20 c.c. of cold 10 per cent. aqueous sodium hydroxide, yielded, on subsequent acidification and extraction with ether, the cyclopropene acid, m. p. 200° . The addition of hydroxylamine hydrochloride (Feist, *loc. cit.*) had no effect on this result.

(G) *Addition of Methyl Alcohol and Ethyl Alcohol to the cycloPropene Esters.*

Methyl 3-Methoxy-3-methylcyclopropane-1:2-dicarboxylate (XLVIII).—Nine grams of normal methyl methylcyclopropene-dicarboxylate were added to a cooled solution of sodium methoxide, prepared from 2 grams of sodium and 30 c.c. of methyl alcohol, and the mixture was immediately poured into 1 litre of dry ether. On filtering from precipitated sodium methoxide, and evaporating the ether, a solid residue was obtained, which crystallised from benzene in short prisms, m. p. 98° (Found: C = 53.1; H = 7.2. $C_8H_{14}O_5$ requires C = 53.4; H = 7.0 per cent.). The same substance was obtained as a by-product in the preparation of the methyl hydrogen salt (below).

Methyl Hydrogen 3-Methoxy-3-methylcyclopropane-1:2-dicarboxylate (XLVII).—The normal cyclopropene ester was added to methyl alcoholic sodium methoxide as in the last experiment, and the mixture kept at the ordinary temperature for one hour and then boiled for two hours. When cool, the solution was poured into dilute hydrochloric acid, and the products extracted with ether, and separated into neutral and acid fractions in the usual way. The neutral extract, on evaporation, gave the above-mentioned dimethyl ester, m. p. 98° . The acid extract yielded a solid residue, which crystallised from xylene in twined prisms, m. p. 136° (Found: C = 51.0; H = 6.7. $C_8H_{12}O_5$ requires C = 50.8; H = 6.4 per cent.). The substance decomposed a few degrees above the m. p., but could be sublimed unchanged in needles. Titration showed it to be a monobasic acid.

3-Ethoxy-3-Methylcyclopropane-1:2-dicarboxylic Acid (XLVI).—This acid, which was obtained as a by-product in the experiments on the interconversion of the three cyclopropene ethyl esters by means of sodium ethoxide (section B), was crystallised from xylene, and thus obtained as small needles, m. p. 156° (*decomp.*) (Found: C = 50.8; H = 6.7. $C_8H_{12}O_5$ requires C = 50.8; H = 6.4 per cent. *M*, by titration = 188; calc. *M* = 188).

Reduction to Normal β -Methylglutaric Acid.—The ethoxy-acid (0.2 gram) was boiled for four hours with 10 c.c. of hydriodic acid (*d* 1.7), and the solution diluted and extracted with ether. The extract was decolorised by means of potassium hydrogen sulphite, dried with sodium sulphate, and evaporated. The residue rapidly set to a cake of crystals, which, after recrystallisation from xylene, were identified as normal β -methylglutaric acid by direct comparison and a mixed melting point determination with a genuine specimen of this acid.

(H) *Oxidation of the cycloPropene Acid by Alkaline Permanganate : Formation of Malonic Acid.*

A solution of the cyclopropene acid (3.55 grams) and sodium carbonate (2.65 grams) in 500 c.c. of water was rapidly stirred mechanically while 1800 c.c. of a 1 per cent. solution of potassium permanganate (corresponding with a little more than seven atoms of available oxygen) were gradually run in. The reduction of the permanganate took place rapidly, almost exactly seven atoms of oxygen being absorbed. The solution was filtered from oxides of manganese, freed from the small excess of permanganate by sulphur dioxide, faintly acidified with hydrochloric acid, evaporated to 200 c.c., then strongly acidified with sulphuric acid, and extracted with ether. On drying and evaporating the ether, a crystalline residue was obtained, which, on recrystallisation from xylene, melted at 132° and had all the properties of malonic acid, with which it was identified by direct comparison and a mixed melting point determination.

In spite of careful search no trace of methylmalonic acid could be isolated.

We desire to thank the Chemical and Royal Societies for grants with the aid of which the expense incurred in this research has been met.

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[Received, December 1st, 1922.]

XLII.—*The Tautomerism of Amidines. Part I.* *2:4- and 2:5-Diphenylglyoxalines.*

By RICHARD BURTLES and FRANK LEE PYMAN.

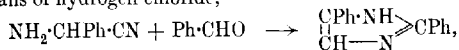
UNSYMMETRICAL amidines, whether open-chain, partly cyclic, or wholly cyclic, exhibit virtual tautomerism, a single substance resulting from reactions designed to prepare the two isomerides. Thus, to give one of many examples, von Pechmann (*Ber.*, 1895, **28**, 874) obtained the same benzoylphenyl-*p*-tolylamidine (I or II) by



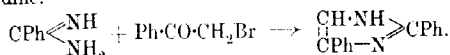
the action of benzoyl-*p*-toluidide iminochloride on aniline and by the action of benzanilide iminochloride on *p*-toluidine. Apparent exceptions to the rule have been reported from time to time, but subsequently disproved. Thus, Meldola, Eyre, and Lane's (*T.*, 1903, **83**, 1185) supposed isomeride of Prager's (*Ber.*, 1885, **18**,

2167) 2-methyl- α -naphthiminazole was shown to be an oxygenated derivative by Otto Fischer (*J. pr. Chem.*, 1907, [ii], **75**, 88), whilst an alleged case of the occurrence of two isomeric forms of a partly cyclic amidine, 1-anilinobenzoxazole, $C_6H_4 \begin{smallmatrix} \text{N} \\ \diagup \diagdown \\ \text{O} \end{smallmatrix} \text{C} \cdot \text{NHPh}$, was disproved by Young and Dunstan (*T.*, 1908, **93**, 1052). There remains, so far as we are aware, but a single uncontradicted example of isomerism of this type amongst amidines, the occurrence of both 2:4- and 2:5-diphenylglyoxalines, which is discussed in the present paper.

The first of the two isomerides to be described was a product, melting at 162° , obtained by Minovici (*Ber.*, 1896, **29**, 2097) either by the condensation of α -aminophenylacetonitrile with benzaldehyde by means of hydrogen chloride,



or by the action of ammonia upon 2:5-diphenylloxazole, and regarded by him as 2:5-diphenylglyoxaline, whilst later Kunczell (*Ber.*, 1901, **34**, 637) described, as 2:4-diphenylglyoxaline, a base melting at 193° , which he prepared by the action of ω -bromoacetophenone upon benzamidine.



We have repeated the preparation of Minovici's base from α -aminophenylacetonitrile and find that it melts at 168° (corr.), and have also confirmed the formation of a base of higher melting point— 194° (corr.)—by Kunczell's method. For brevity, these bases are distinguished below as M and K, respectively. Repetition of the analyses of both bases gave figures in good agreement with those required for diphenylglyoxaline, and it remained to determine whether they were isomeric or polymorphic forms of the same substance. The main results of the investigation were as follows: The two bases yield identical salts with any given acid, from which the recovered base is M. The base K is obtained almost consistently by Kunczell's method, but on heating for a short time in alcoholic solution, it is converted into M. In no case has M been converted into K. Saturated alcoholic solutions of the much more readily soluble base M failed to deposit the sparingly soluble base K on inoculation. In the region of the melting point, M is the stable compound. A mixture of equal parts of M and K melts at a temperature, about 174 — 175° , intermediate between their melting points.

These results lead to the conclusion that the compounds are not polymorphic but isomeric, and represent the 2:4- and 2:5-di-

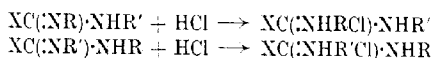
phenylglyoxalines. It does not, however, seem to us to be possible to judge from their methods of formation which is the 2:4- and which the 2:5-isomeride.

The formation of a single salt by the action of an acid upon the two bases is doubtless due to the fact that the ions of the salts of the two bases are not position-isomerides, but—if they differ at all, as would appear from the usual conventional formulæ given below—



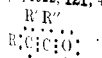
valency-isomerides. In other words, whilst the bases themselves are isomeric, the basic ions are tautomeric in Laar's sense of the word. This leads us to the view that the previous attempts of von Pechmann and others to synthesise the two isomeric forms of other amidines have necessarily failed wherever the bases have been converted into their salts. For we hold that the formation of salts or alkyl salts of amidines is due to the addition of the acid or alkyl salt to the doubly-linked nitrogen atom, and thus find ourselves in agreement with Young and Crookes (T., 1906, **89**, 59), but in opposition to the views of von Pechmann (*Ber.*, 1895, **28**, 2362) and Cohen and Marshall (T., 1910, **97**, 328), who regard the formation of an alkyl derivative $\text{X} \cdot \text{C} \begin{smallmatrix} \text{NR} \\ \ll \\ \text{NR}'\text{Alkyl} \end{smallmatrix}$ as an indication that the amidine has reacted in the form $\text{X} \cdot \text{C} \begin{smallmatrix} \text{NR} \\ \ll \\ \text{NHR}' \end{smallmatrix}$.

In support of our view, we may point out that amidines are monacidic bases, that obviously the acid or alkyl salt would combine with the basic nitrogen atom, and that a comparison of amidines, $\text{R} \cdot \text{C}(\text{NH}) \cdot \text{NH}_2$, with the basic imino-ethers, $\text{R} \cdot \text{C}(\text{NH}) \cdot \text{OEt}$, on the one hand, and the non-basic acid amides, $\text{R} \cdot \text{CO} \cdot \text{NH}_2$, on the other, leaves no doubt as to which of the nitrogen atoms of amidines is to be regarded as basic. It appears then that the conversion of the two isomeric forms of an amidine into the salts may be represented as follows:

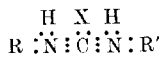


and that the two salts have a common ion and therefore are identical. The common ion* can be represented on an electronic

* It should be pointed out that Lapworth's view of the mechanism of the desmotropism of ethyl acetoneacetate (*Mem. Manchester Phil. Soc.*, 1920, **64**, 1, 13), when interpreted upon an electronic basis as suggested by him later (T., 1922, **121**, 424), leads to a similar expression for a common ion, that is,



basis, after Kermack and Robinson (T., 1922, **121**, 427) by the formula



Clearly, the identity of the methiodides of 1:4- and 1:5-dimethylglyoxalines (Pyman, T., 1910, **97**, 1814) is due to a similar cause.

In the case of the diphenylglyoxalines, the production of the labile form of higher melting point by Kunckell's method is rendered possible by the alkalinity of the reaction mixture owing to the excess of benzamidine employed, and consequent avoidance of ionisation.

EXPERIMENTAL.

Kunckell's Base.—The benzamidine liberated from 14 grams of the hydrochloride by means of sodium hydroxide was extracted with 30 grams of chloroform, 6 grams of *o*-bromoacetophenone were added, and the product was boiled for four hours under reflux. After distillation of the solvent, there remained a brown, gummy mass, which was extracted three times with warm water, and then mixed with benzene, when a yellow, crystalline product remained undissolved. This was boiled with dilute aqueous sodium carbonate to convert any salt to base, and gave from 5 to 6 grams of a pale yellow, crystalline powder melting at 191° or 192°. The yield of crude product is thus nearly theoretical, but on crystallising the product from alcohol there were obtained on the average only 2.5 grams of base melting at 193°, and on concentration of the mother-liquors 1.6 grams of base melting at 167°. Similar results were obtained in six repetitions of this experiment, but on two occasions when the reaction proceeded abnormally small quantities of the base of lower melting point were obtained and none of the base of higher melting point.

On recrystallising the base melting at 193° from alcohol, it separated in well-formed, colourless prisms which melted at 194° (corr.) (Found: C = 81.6; H = 5.8; N = 12.9: Calc., C = 81.8; H = 5.5; N = 12.7 per cent.). After heating for fifteen minutes with alcohol on the water-bath, it was converted into a base melting at 168° (corr.) which was identical with Minović's base (Found: C = 81.6; H = 5.8 per cent.).

Minović's Base.—The crude α -aminophenylacetonitrile resulting from the action of alcoholic ammonia on mandelonitrile was dissolved in ether, filtered to remove α -benzylideneaminophenylacetonitrile, and condensed with benzaldehyde by means of dry hydrogen chloride, when the diphenylglyoxaline melting at 168° (corr.) was obtained in very poor yield.

Behaviour of the Salts.—The two bases give the same salt with any given acid. The hydrochloride, for which Minovici records the melting point 273° and Kuncell 262° , was prepared by passing dry hydrogen chloride through ethereal solutions of the two bases M and K at 0° , when the crude products melted at 274 – 275° and 272 – 274° , respectively. On warming these salts with aqueous sodium carbonate, the base M was obtained in each case.

The *hydrogen oxalates* were precipitated on the addition of a cold concentrated alcoholic solution of oxalic acid to cold concentrated alcoholic solutions of the bases M and K, and melted at 225° and 227° , respectively, a mixture of equal parts of the two melting at 225° .

The *acetates* were prepared by allowing cold concentrated solutions of the bases (M and K) in glacial acetic acid to evaporate spontaneously, when long, silky needles, which melted at 95° and 96° , respectively, separated. A mixture of the salts from the two sources melted at 95° . This salt contains $\frac{1}{2}\text{H}_2\text{O}$ (Found: C = 69.9; H = 6.1; N = 9.6; loss at 100° = 22.7. $\text{C}_{15}\text{H}_{12}\text{N}_2\cdot\text{C}_2\text{H}_3\text{O}_2\cdot\frac{1}{2}\text{H}_2\text{O}$ requires C = 70.6; H = 5.9; N = 9.7; loss of $\text{C}_2\text{H}_3\text{O}_2\cdot\frac{1}{2}\text{H}_2\text{O}$ = 23.9 per cent.).

The residue left after heating the acetate of the base M melted at 167° , and the residue left after heating the acetate of the base K melted at 160° .

Some evidence was obtained that the change $\text{K} \rightarrow \text{M}$ proceeds only slowly in the absence of mineral acid; thus a quantity of K was dissolved in glacial acetic acid, diluted with water, and basified at once with ammonia, when the precipitate which gradually solidified softened from 170° and melted at about 185 – 192° , but after crystallisation from alcohol it melted at 167° .

Cryoscopic Determinations.

The very slight solubility of the bases in benzene or aniline prevented the use of these solvents in determining the molecular weights of the bases by the cryoscopic method, but determinations were made in glacial acetic acid, when high results averaging 276 for K and 260 for M were obtained. These results are no doubt vitiated by the formation of the acetate, and the same criticism applies to attempts to distinguish between isomerism and polymorphism by Sidgwick's method (L., 1915, 107, 673) using the same solvent. The results, however, are given below, because, apart from this criticism, they are in opposition to our view that the compounds are isomeric. Thus, saturation of glacial acetic acid with M gave in two experiments $\Delta -3.5^{\circ}$ and -3.8° ; on the addition of K a rise of $+0.7^{\circ}$ and 0.8° occurred, whilst saturation of glacial acetic

acid with K gave $\Delta -2.5^\circ$ and -2.8° , and with addition of M a further depression of 0.8° and 0.9° .

Solubilities in Alcohol.

The finely powdered bases in excess were well shaken with absolute alcohol, kept in a thermostat for three hours in the case of K and one night in the case of M, and filtered. The solubility was then determined by evaporating weighed portions (about 2 c.c.) of the solutions and weighing the residues. To another portion of the solution of the more soluble base M, some of the finely powdered base K was added and the mixture was well shaken in the thermostat for half an hour, when the amount of material in solution was again determined.

The results were as follows :—

Temperature.	Solubility in grams per 100 grams of absolute alcohol.		
	K(194°).	M(168°).	M + K.
0°	3.49, 3.63	11.34	10.66, 10.68
10	4.39, 4.41	14.77	14.81, 15.04
25	[5.9 at 27°]	15.98	16.47, 16.49
36		23.6, 23.7	23.3, 23.4

The results must be regarded as only approximate in view of the small quantities of the solutions employed. They do not show consistently that saturated solutions of M will dissolve K, as one would expect in the case of substances differing in the liquid state, but they show plainly that addition of K to saturated solutions of M does not cause (or at the temperatures 0° and 36° causes to only a very slight extent) deposition of the more sparingly soluble form.

Another experiment on the behaviour of the bases in alcoholic solution follows. Hot concentrated alcoholic solutions of the two bases were filtered, and each filtrate was divided into two parts, one of which was inoculated with K, the other with the base M, when it was found that the solutions of K deposited crystals melting at 194° (corr.) in both cases, whilst the solutions of M deposited crystals melting at 168° (corr.) in both cases.

Behaviour on Heating.

The base M was heated in a small test tube surrounded by liquid paraffin, and gave a perfectly clear solution at 169° . The temperature was now maintained at 171 – 172° for half an hour, and a trace of the base K was added, but did not cause crystallisation. The liquid was now allowed to cool to 120° , and stirred to cause crystallisation. The melting point of the resolidified mass was again determined, when it began to soften at 160° and gave a clear

liquid at 171° . The base M is thus stable in the region of the melting point.

The base K was similarly heated for half an hour at 171 – 172° , when it underwent no change. On raising the temperature, it began to melt at 189° , but was not clear until a temperature of 194° was reached. The liquid was now allowed to cool to 120° and stirred to promote crystallisation, and the melting point was redetermined, when it was found that the substance began to soften at 160° , but was not clear until 186° . After cooling once more and heating again, the substance softened at 160° and was quite clear at 172° . The base K is thus unstable in the region of the melting point.

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[Received, January 18th, 1923.]

XLIII.—*The Tautomerism of Amidines. Part II. The Alkylation of Open-chain Amidines.*

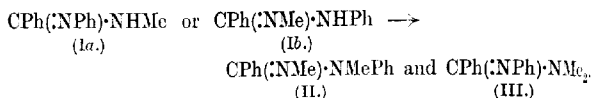
By FRANK LEE PYMAN.

THE results of alkylating unsymmetrical open-chain amidines containing the group $\cdot\text{C}(\text{NR}')\cdot\text{NHR}$ or $\cdot\text{C}(\text{NR})\cdot\text{NHR}'$ by heating with alkyl salts are stated to depend on the nature of the groups R and R'. Where R and R' are similar in character, for example, phenyl and *o*-tolyl or phenyl and β -naphthyl, a mixture of the two possible alkyl derivatives is obtained in approximately equal amounts, but where the two groups differ in character, for example, phenyl and methyl, or ethyl and menthyl, only a single alkyl derivative has been isolated, in which the alkyl group is attached to the less basic nitrogen atom (Marckwald, *Annalen*, 1895, **286**, 343; von Pechmann, *Ber.*, 1895, **28**, 869, 2362; 1897, **30**, 1779; von Pechmann and Heinze, *ibid.*, 1783; Cohen and Marshall, *T.*, 1910, **97**, 328).

The isolation of only one of the two possible alkyl derivatives in these cases has led to the view that only one is formed, but in the present author's opinion this view is incorrect.

It was shown recently (Pyman, *T.*, 1922, **121**, 2616) that whereas methylation of 4-methylglyoxaline leads to the 1:4- and 1:5-dimethylglyoxalines in the proportion of 2:2:1, the methylation of 5-nitro-4-methylglyoxaline leads to the formation of the 1:4- and 1:5-dimethylnitroglyoxalines in the proportion of 233:1. In the latter case, it was only the fortunate difference in physical properties between the two isomeric alkyl derivatives that rendered possible the isolation of the isomeride produced in

smaller quantity. Consequently, it seemed not improbable that the isolation of single alkyl derivatives by the authors cited above was due to the experimental difficulties of isolating the isomeride produced in smaller quantity rather than to its absence, and this view received some support from their experimental records. It was decided, therefore, to repeat the alkylation of an unsymmetrical open-chain amidine, which had been stated to yield a homogeneous alkyl derivative, and benzenylphenylmethylamidine (Ia or Ib) was selected as a typical example.



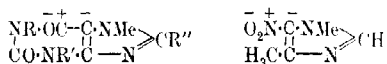
According to von Pechmann (*loc. cit.*), the methylation of this base by means of methyl iodide at 100° yields methylphenylamidobenzenylmethylimidine (II) as a homogeneous product, although the yield is not stated numerically. Repetition of this alkylation has now shown that whilst methylphenylamidobenzenylmethylimidine is certainly the main product of the reaction, it is accompanied by a small proportion of the isomeric dimethylamidobenzenylphenylimidine (III), which von Pechmann prepared by the action of benzanilide iminochloride on dimethylamine, the relative yields of the two isomerides being approximately 15:1.

From this result the conclusion is drawn that the alkylation of open-chain, as well as cyclic (compare Pyman, *loc. cit.*), amidines leads to a mixture of the two isomeric alkyl derivatives in proportions which depend on the relative character of R and R', the greater the difference in character between R and R', the greater being the difference in yield of the two isomerides.*

Further investigations of the relative amounts of the isomeric alkyl derivatives produced by the alkylation of amidines are contemplated, and it is hoped that these may throw some light on the tautomerism of amidines and also on the relative influence of the substituents R and R'. Further discussion of the reaction, however, is postponed until more material has been accumulated. In the meantime, it is desired to direct attention to the important influence of carbonyl oxygen in the pyrimidine ring on the results

* This appears to be the case also in the alkylation of unsymmetrical diazoamino-compounds, $\text{R}\cdot\text{NH}\cdot\text{N}:\text{N}\cdot\text{R}'$, for in many cases where R and R' were substituted phenyl groups Meldola and Streatfeild obtained mixtures of the two isomeric alkyl derivatives in more or less equal amounts, whereas von Walther and Griesshammer (*J. pr. Chem.*, 1915, [ii], 92, 209) found that the methylation of *p*-toluenediazocyanodiamide gave mainly the methyl derivative, $\text{CN}\cdot\text{NH}\cdot\text{C}(\text{NH})\cdot\text{N}_2\cdot\text{NMe}\cdot\text{C}_6\text{H}_4\cdot\text{Me}$.

of alkylating the glyoxaline ring in purines. Whereas 2:6:8-trichloropurine gave with methyl iodide and aqueous potassium hydroxide a mixture of the 7- and 9-methyl derivatives (E. Fischer, *Ber.*, 1897, **30**, 2224), the methylation of derivatives of xanthine has not afforded 9-methyl derivatives (E. Fischer, *Ber.*, 1899, **32**, 435); thus the silver salt of 8-chlorotheophylline and methyl iodide gave a 50 per cent. yield of the 7-methyl derivative, 8-chloro-caffeine (E. Fischer and Ach, *Ber.*, 1895, **28**, 3135), whilst the methylation of 8-chloro-3-methylxanthine with either methyl iodide or potassium methyl sulphate in alkaline solution gave again the 7-methyl derivative, 8-chlorotheobromine, in "quite satisfactory" yield (Fischer and Ach, *Ber.*, 1898, **31**, 1980). In view of the moderate yields of the 7-methyl derivatives in these cases it may be surmised that here also the 9-methyl derivatives were formed in small proportion. The predominant formation of the 7-methyl derivatives of xanthines recorded above may be compared directly with the results of methylating 5-nitro-4-methylglyoxaline on the assumption of a similar distribution of polarity induced by the oxygen atoms, which is indicated vaguely by the following formulæ of the principal products of methylation.



EXPERIMENTAL.

Methylation of Benzenylphenylmethylamidine.—Twenty grams of benzenylphenylmethylamidine, which melted at 135–136° (corr.) (von Pechmann gives 134°), and 20 c.c. of methyl iodide were heated for three hours at 100°. After removing excess of methyl iodide, the base was liberated by sodium hydroxide and collected by means of ether, when 20 grams of oil were obtained. This was mixed with a hot solution of 22 grams of picric acid in 200 c.c. of alcohol and gave (A) 26.5 grams of picrate, melting at 173°, (B) 5.4 grams of picrate, melting at 140–155°, and a final mother-liquor, from which the base was regenerated. There were thus obtained 2 grams of oil which on the addition of light petroleum deposited first 0.2 gram of the original material, melting at 125–130°, and then on concentration 0.48 gram of dimethylamidobenzenylphenylimidine, which softened at 65° and melted at 70–71°, leaving a mother-liquor M. The product A on crystallisation from 200 c.c. of alcohol gave 24.5 grams of methylphenylamidobenzenylmethylimidine picrate which melted at 174–176° (corr.) (von Pechmann gives 174°). The mother-liquor from this was evaporated dry and the residue combined with B and converted

into the base, which was separated by light petroleum into 1.5 grams of the original material, melting at 134° , and 1.5 grams of oil. This was combined with M and converted into the picrate, giving 3.25 grams of crude methylphenylamidobenzenylmethylimidine picrate, melting at $165-170^{\circ}$, which after two crystallisations from alcohol gave 2.4 grams of the pure substance, and a mother-liquor from which the base was regenerated. It amounted to 0.8 gram and on treatment with light petroleum gave 0.1 gram of the original material melting at $125-130^{\circ}$, and 0.42 gram of dimethylamidobenzenylphenylimidine, which softened at 65° and melted at $70-71^{\circ}$. The yields of the two methyl derivatives, allowing for the recovered material, amount to 68.5 and 4.6 per cent. of the theoretical, respectively.

Dimethylamidobenzenylphenylimidine melted at $72-73^{\circ}$ (corr.) after crystallisation from light petroleum (von Pechmann gives $73-74^{\circ}$), and its identification was confirmed by the preparation of the hydriodide, which melted at 200° (corr.), and picrate, which melted at $126-127^{\circ}$ (corr.) (von Pechmann gives 196° and 126° , respectively).

The identification of methylphenylamidobenzenylmethylimidine was confirmed by the preparation of the hydriodide, which melted at $191-192^{\circ}$ (corr.) (von Pechmann gives 190°), but the base melted at $65-66^{\circ}$ (corr.), several degrees higher than the temperature— 56° —recorded by von Pechmann.

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[Received, January 18th, 1923.]

XLIV.—The Quantitative Absorption of Light by Simple Inorganic Substances. Part II. The Chlorides of Arsenic, Antimony, and Bismuth.

By ALEXANDER KILLEN MACBETH and NORAH IRENE MAXWELL.

THE study of the quantitative absorption of light by simple inorganic salts was undertaken some time ago, the object of the work being to determine if any connexion existed between the molecular extinction-coefficients of members of the same group of elements and their atomic numbers or atomic weights; and subsequently to see if the extinction-coefficient is a periodic function when the elements are reviewed as a whole.

The results obtained when examining the halides of the alkali metals and hydrogen have already been described (Brannigan and Macbeth, T., 1916, 109, 1277). It was found that, in general,

the molecular extinction-coefficient of these salts increased with the increase of atomic weight, and the effect was specially marked in the case of the iodides. The observed extinction-coefficients were small, lying between the values 0.05 and 0.5. In the present cases, the values are much greater, the experimental figures covering a range from 5 to 12,000.

It is evident, therefore, that in the examination of the different groups of inorganic salts it will be necessary to employ solutions of considerably different concentration. In the case of the alkali chlorides, for example, 4*N*-solutions were found to be of suitable concentration; with bismuth chloride, dilution to an *N*/10,000-solution was necessary before the absorption could be satisfactorily examined. On this account, it is a matter of importance to determine if the molecular extinction-coefficient as determined by the method adopted in this work is independent of the actual dilution of the solutions, and to ascertain if the values obtained at different concentrations are in agreement with Beer's law.

A Hilger spectrophotometer was used in the measurements, and the molecular extinction-coefficients were derived from the expression $\log(I/I_0)/dc$, where *I* and *I*₀ have their usual significance, *d* is the length of solution, in centimetres, through which the light passes, and *c* is the concentration in gram-molecules per litre. A high-tension spark between nickel electrodes was used as the source of light; the intensity of this light remained fairly constant throughout the experiments, and the arrangement was approximately a point source. The ratio $\log I/I_0$ was varied by means of an adjustable rotating sector, and the calibration of the instrument for the different sector openings was carried out by a preliminary series of photographs with a standardised test-plate, supplied by the makers. The following values were obtained:

Sector opening.	Log I/I_0	Sector opening.	Log I/I_0	Sector opening.	Log I/I_0
0.1	0.220	0.6	0.550	1.1	0.900
0.2	0.293	0.7	0.640	1.2	1.050
0.3	0.350	0.8	0.700	1.3	1.110
0.4	0.425	0.9	0.770	1.4	1.265
0.5	0.480	1.0	0.825	1.5	1.380

From the above values it is seen that limits of the molecular extinction-coefficients of any absorbing substance must lie within the ratio 1:6 (220:1380) if the absorption over the visible and ultra-violet regions is to be completely examined at one particular dilution; and with very absorptive substances this range will not be sufficient to cover more than a limited region of the spectrum. Azobenzene is an example of a substance of this type, and examination of a solution of *N*/20,000-strength covers only the region of

TABLE I.

Azobenzene. Band region λ 4370.

Concentration N/500.	1 cm. cell.	Concentration N/1000.	2 cm. cell.
λ .	A.	λ .	A.
378, 500	175	378, 500	175
370, 384, 496	212	371, 384, 497	212
368, 389, 495	240	366, 391, 494	240
365, 394, 488	275	365, 391, 484	275
363, 397, 483	320	363, 386, 482	320
362, 400, 478	350	361, 402, 476	350
362, 405, 468	385	360, 407, 468	385
361, 410, 463	412	360, 410, 460	412
361, 413, 458	450	360, 415, 456	450
361, 415, 456	525	359, 418, 453	525
360, 420, 453	550	359, 423, 450	550
359, 423, 450	632	359, 426, 450	632
437	690	437	690

Concentration N/2000. 4 cm. cell.

λ .	A.	λ .	A.
378, 500	175	360, 407, 463	412
370, 384, 498	212	360, 408, 458	450
367, 391, 493	240	359, 412, 455	525
362, 394, 481	275	359, 418, 453	550
362, 397, 480	320	359, 423, 448	632
361, 400, 472	350	437	690
360, 405, 467	385		

TABLE II.

Azobenzene. Band region λ 3210.

Concentration N/20,000.	1 cm. cell.	Concentration N/40,000.	2 cm. cell.
λ .	A.	λ .	A.
249	5,860	250	5,860
241, 262	7,000	242, 263	7,000
220, 238, 269	8,500	220, 237, 273	8,500
222, 235, 275, 344	9,600	223, 235, 275, 341	9,600
225, 233, 280, 340	11,000	225, 232, 281, 339	11,000
229, 284, 339	12,800	229, 285, 338	12,800
288, 338	14,000	290, 337	14,000
293, 335	15,400	295, 335	15,400
298, 334	16,500	300, 334	16,500
303, 330	18,000	306, 331	18,000
309, 329	21,000	310, 328	21,000
321	22,000	321	22,000

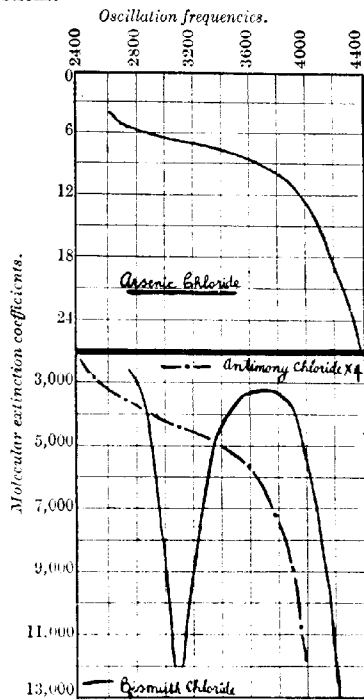
Concentration N/80,000. 4 cm. cell.

λ .	A.	λ .	A.
250	5,860	290, 337	14,000
241, 262	7,000	294, 336	15,400
218, 237, 272	8,500	300, 335	16,500
222, 235, 276, 340	9,600	305, 332	18,000
225, 232, 281, 340	11,000	311, 327	21,000
229, 286, 339	12,800	321	22,000

wave-lengths extending from 3780—5000 Å.U. Measurements of the absorption of solutions of different concentrations are therefore necessary in such a case, and it was decided to examine the absorption of azobenzene in detail before proceeding further with

the study of the simple inorganic salts. Azobenzene provides a suitable range of dilutions to test the spectrophotometric method in the light of Beer's law: and is a good case to examine with the view of finding if the graph connecting molecular extinction-coefficients and oscillation frequencies is continuous over the whole range of dilutions. The method was found to be satisfactory as regards both these questions.

The azobenzene used in the work was repeatedly crystallised from alcohol until it melted sharply at 68° . Alcoholic solutions were used throughout, and a cell of alcohol was fixed in front of the variable sector in order to introduce a correction for absorption by the solvent. Azobenzene has two principal bands in its absorption spectrum, and these regions were especially examined. The first band—with its head at $\lambda 4370$ —was examined at dilutions of $N/500$, $N/1000$, and $N/2000$: the second band—with its head at $\lambda 3210$ —was studied in solutions of $N/20,000$, $N/40,000$, and $N/80,000$ strength. The values obtained are expressed in Tables I and II, where $A = \log (I/I_0)/dc$.



From the results recorded above, it is seen that the molecular extinction-coefficient remains the same for a particular wavelength, whether a concentrated or a dilute solution is employed. The value therefore depends only on the number of molecules of solute through which the light is passed, and no dilution effect will be noted if a compensation cell of solvent is interposed in the path of the light falling on the variable sector. Beer's law is therefore obeyed in measurements with the spectrophotometer.

The absorptions shown by a 1 cm. cell containing $N/1000$ - and O^*

$N/10,000$ -azobenzene were also examined, to cover the range of general absorption lying between the two bands already dealt with. On plotting the values of molecular extinction-coefficients obtained over the whole series of dilutions against oscillation frequencies, a continuous graph is obtained.

It will also be noted that the examination of the absorption of azobenzene by the spectrophotometer reveals the presence of a third band in the extreme ultra-violet region—with its head at $\lambda 2290$. This shallow band has not been observed in previous work, and this is probably accounted for by the fact that the absorption due to the solvent could not be eliminated—even a 1 cm. cell of alcohol is found to be absorptive in this region (compare Crymble, Stewart, and Wright, *Ber.*, 1910, **43**, 1188; Purvis, T., 1914, **105**, 590; Baly and Hampson, T., 1915, **197**, 248).

Arsenic Trichloride.

The trichloride was prepared by the action of chlorine on the metal (Dumas, *Ann. Physik*, 1827, [i], **9**, 308). It was purified by distillation and the fraction, b. p. 134° , was collected. A solution of the chloride in N -hydrochloric acid was prepared, and a concentration of $N/100$ of the chloride was found to be of suitable strength. A compensation cell of N -hydrochloric acid was introduced during the measurement of the absorption, and the following values were determined. The substance shows general absorption only, the molecular extinction-coefficients having a range from 5–30.

TABLE III.

Arsenic Trichloride.

Concentration $N/100$.				4 cm. cell.	
λ .	A .	λ .	A .	λ .	A .
357	5.5	248	13.750	232	22.5
301	7.325	243	16.00	228	26.25
275	8.750	240	17.50	227	27.5
259	10.625	237	19.25		
253	12.00	235	20.625		

Antimony Trichloride.

The trichloride was prepared from the metal by Hengsen's method (*Rec. trav. chim.*, 1890, **9**, 301). It was purified by fractional distillation and collected at the correct boiling point. An $N/100$ -solution in N -hydrochloric acid was prepared, but dilution to $N/10,000$ with the same solvent was necessary before a suitable concentration was obtained. The substance shows general absorption only; the molecular extinction-coefficients having a range from 600–3000. The values determined are given below:

TABLE IV.
Antimony Trichloride.

Concentration N/10,000. 4 cm. cell.					
λ .	A .	λ .	A .	λ .	A .
417	550	283	1,375	257	2,250
391	732.5	270	1,600	253	2,625
366	875	266	1,750	251	2,750
320	1,062	262	1,925		
302	1,200	259	2,062		

Bismuth Trichloride.

This chloride was prepared from the pure metal by Muir's method (T., 1876, 29, 144). It was fractionally distilled under reduced pressure, but as the boiling point was too high to record the chloride was converted into the oxide, and found to be pure (1.60 grams gave 1.0565 grams Bi_2O_3 , which corresponds with a theoretical 1.597 grams of chloride). An N/100-solution in N-hydrochloric acid was prepared, but dilution to N/10,000 was necessary to give a suitable concentration. The absorption is characterised by very strong selective action, a deep band with its head at $\lambda 3250$ being observed. The molecular extinction-coefficients, which cover a range from 2000—12,000, are given below.

TABLE V.
Bismuth Trichloride.
Concentration N/10,000. 1 cm. cell.

λ .	A .	λ .	A .
357	2,930	335, 307, 244	7,700
350, 282, 260	3,500	334, 309, 243	8,250
347, 292, 254	4,250	332, 312, 242	9,000
344, 296, 252	4,800	329, 316, 240	10,500
342, 299, 250	5,500	327, 318, 239	11,000
338, 303, 247	6,400	237	12,650
337, 305, 246	7,000		

The values of the molecular extinction-coefficients observed in the arsenic-antimony-bismuth group show that this factor increases with increase of the atomic weight of the element. The selective absorption by the bismuth is remarkable, but it would be unwise to submit any explanation of this action until further information is collected. It is hoped that after further groups of elements have been examined some numerical connexion between absorption and atomic weight will be deducible, but at the present stage of the work no clear relationship can be traced.

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[Received, November 30th, 1922.]

XLV.—*The Influence of Papaverine on the Optical Activity of Narcotine in Acid Solution.*

By HAROLD EDWARD ANNETT.

NARCOTINE in acid solution is dextrorotatory, whilst the free base, dissolved in chloroform, toluene, or alcohol, is lævorotatory. Papaverine is optically inactive. It would seem, therefore, that narcotine could be estimated in admixture with papaverine by a polarimetric method. It was found that although papaverine is inactive in acid solution, yet when it is added to an acid solution of narcotine the optical activity of narcotine is considerably diminished.

EXPERIMENTAL.

A Hilger polarimeter, fitted with a D. V. spectroscope eyepiece attachment, was used for the investigation. The readings refer to the green mercury line unless otherwise specified. The alkaloids used were of a high degree of purity, kindly provided by Mr. G. Whiffen. The narcotine and papaverine melted sharply at 172.75° (175.8° corr.) and 146.75° (148.5° corr.), respectively.

Series I.—Four grams of narcotine and 1 gram of papaverine were dissolved each in 100 c.c. of 1 per cent. sulphuric acid, and from these solutions mixtures were made up for polarimetric observation. A similar set of solutions was prepared in which 1 per cent. hydrochloric acid was used instead of 1 per cent. sulphuric acid.

Series II.—Two grams of narcotine were dissolved in 100 c.c. of 1 per cent. sulphuric acid. The rotation of the solution in a 200-mm. tube was measured. Three portions, each of 25 c.c., were removed and to these portions 0.125, 0.250, and 0.500 gram, respectively, of papaverine were added, and the rotations again observed in the 200-mm. tube. The results of these two series of experiments are shown in the attached table.

Series No	Concentration. Grams per 100 c.c. of acid.		Reading in 200-mm. tube at 31°.	
	Narcotine.	Papaverine.	H ₂ SO ₄ 1 %.	HCl. 1 %.
I	2.0	0.0	+ 2.61°	+ 2.23°
	0.0	0.5	+ 0.02	+ 0.02
	2.0	"	+ 2.24	+ 1.76
	2.0	0.0	+ 2.59	—
II	"	0.5	+ 2.19	—
	"	1.0	+ 2.00	—
	"	2.0	+ 1.69	—
	"	3.0	+ 1.49	—
	"	4.0	+ 1.45	—

The readings of series I show that (1) papaverine is optically inactive in 1 per cent. sulphuric or hydrochloric acid, but when present in solution with narcotine it considerably affects the optical activity of the latter, (2) narcotine shows a greater degree of optical activity in 1 per cent. sulphuric acid than in 1 per cent. hydrochloric acid, and (3) the effect of papaverine on the optical activity of narcotine is relatively much greater in solution in hydrochloric acid than in sulphuric acid.

The results with the second series show that each additional amount of papaverine diminishes the rotation due to narcotine until the ratio of papaverine to narcotine is 3:2, and a further increase of this ratio to 4:2 has much less effect.

Series III.—It appeared of interest to determine the effect of adding a strong base such as sodium hydroxide to an acid solution of narcotine, on its optical activity. A solution of 4 grams of narcotine in 100 c.c. of 2 per cent. sulphuric acid was prepared and from this the following solutions were made up. (a) Twenty-five c.c. were diluted to 50 c.c. with water, (b) 25 c.c. were diluted to 50 c.c. with water after the addition of 10 c.c. of *N*/10-sodium hydroxide, (c) 25 c.c. were diluted to 50 c.c. with *N*/10-sodium hydroxide. These solutions gave the following readings in a 200-mm. tube: $+2.56^\circ$, $+2.61^\circ$, and $+2.65^\circ$, respectively. The effect of adding sodium hydroxide is therefore quite different from that of addition of papaverine.

Series IV.—The effect of papaverine in diminishing the optical activity of narcotine in acid solution might be explained by the formation of associated molecules of the two alkaloids. It was therefore of interest to observe the effect of dilution.

To 40 c.c. of solution (a) under Series III above was added 0.40 gram of papaverine and this gave a reading of $\div 2.19^\circ$. Ten c.c. of this solution were diluted to 50 c.c. with water and then gave a reading of $\div 0.50^\circ$. If dilution had no effect, its reading should have been $\div 2.19^\circ/5 = \div 0.44^\circ$. Errors in reading could not have accounted for so large a difference.

It would seem that dilution had almost nullified the effect of papaverine on the optical activity of narcotine, since solution (a) itself, containing only narcotine, gave a reading of $\div 2.56^\circ$, and on dilution five times would be expected to give a reading of $\div 0.51^\circ$, which is practically the figure obtained in the diluted solution of narcotine and papaverine.

Series V.—It remained to determine whether a similar effect would be observed when the free bases were dissolved in an inactive solvent, such as toluene. The table sets out the results.

Conc.	Grams per 100 c.c. of toluene.	Reading in 200-mm. tube at 31°.
Narcotine.	Papaverine.	
1-333	0-00	- 4-83°
0-00	0-50	± 0-00
1-333	0-50	- 4-82
1-333	1-00	- 4-84

It is thus seen that papaverine is inactive and that when the free bases are present together in solution in an inactive solvent papaverine exercises no effect on the optical activity of narcotine.

Series VI.—Since narcotine is levorotatory in alcoholic solution and dextrorotatory in acid solution, it appeared of interest to determine the effect of mixing an alcoholic solution of narcotine with a solution of narcotine in acid. The result was somewhat unexpected.

One gram of narcotine was dissolved in 100 c.c. of 1 per cent. hydrochloric acid (solution A).

One gram of narcotine was dissolved in 250 c.c. of 90 per cent. ethyl alcohol (solution B).

The rotation of each solution was then observed in a 200-mm. tube using the green line of the mercury arc. The readings obtained were + 1-14° and - 1-63°, respectively, at a temperature of 29°, whence $[\alpha]_{D}^{29} = + 57-0^{\circ}$ and - 203-75°. Twenty-five c.c. of A were then mixed with 25 c.c. of B and gave a reading of + 1-43° in the 200-mm. tube at 33°, and since $c = 0-7$ for this mixed solution, $[\alpha]_{D}^{33} = + 102-14^{\circ}$.

It is thus seen that although narcotine is levorotatory in alcoholic solution and dextrorotatory in acid solution, yet in acid alcohol solution the alkaloid is much more dextrorotatory than in acid solution alone. Hesse (*Annalen*, 1875, **176**, 195) records a similar result, but at the time my experiment was made his work had been overlooked.

The Specific Rotation of Narcotine.

During the course of the above work the specific rotation of narcotine was determined in toluene, ethyl alcohol, sulphuric acid, and hydrochloric acid, and the measurements were made for the sodium flame, and for the yellow and green lines of the mercury arc. For the latter two readings, the D. V. spectroscope eyepiece attachment was used. The results are set out below.

Solvent.	Toluene.	Ethyl alcohol. 90 %.	Chloroform.	H ₂ SO ₄ . 1 %.	HCl. 1 %.
Conc. Grams per 100 c.c.	2	0-4	2-0	2-0	1-0
Temp.	32°	31°	33°	32°	29°
$[\alpha]_{D}^{29}$	- 148-75°	—	- 198-0°	+ 57-25°	+ 50-0°
$[\alpha]_{D}^{33}$	154-5°	—	- 206-5°	—	+ 52-2°
* $[\alpha]_{Hg}^{yellow}$	— 162°	- 203-75°	- 242-25°	+ 65-2°	+ 56-5°
$[\alpha]_{Hg}^{green}$					

The toluene and chloroform used were A.R. reagents, freshly supplied by Messrs. The British Drug Houses Limited. Hesse (*loc. cit.*) gives $\alpha_D^{25} = -207.35^\circ$ for narcotine in chloroform solution ($c = 2$ to 5). For narcotine in hydrochloric acid solution, he gives $\alpha_D^{25} = +50.0^\circ$, a figure exactly agreeing with that found by the author.

Summary.

1. Papaverine is shown to be optically inactive both in acid solution and in an inactive solvent.

2. The specific rotation of narcotine in various solvents for the sodium flame and for the yellow and green lines of the mercury arc have been determined.

3. Although papaverine is itself inactive, yet when it is added to a solution of narcotine in 1 per cent. sulphuric acid it causes a rapid diminution of the optical activity of the solution. The effect increases with each successive addition of papaverine until the ratio of papaverine to narcotine is 3 : 2, after which an increase in the ratio to 4 : 2 has only a slight, if any, influence. The effect was observed in solutions containing 2 per cent. of narcotine, and when the solutions were diluted to 0.4 per cent. the effect was much less marked.

It would appear that in acid solution narcotine and papaverine form associated molecules, which become dissociated on greater dilution.

4. The optical activity of narcotine is less in hydrochloric acid than in sulphuric acid, but on the other hand the effect of papaverine on the optical activity of narcotine is relatively much greater in the former than in the latter.

5. No effect is observed when the free bases are present together in an inactive solvent such as toluene, so that it would seem that acid is necessary in order to cause an alteration in the structure of the narcotine molecule. That such alteration must take place in acid solution is indicated by the fact that the free base is levorotatory in an inactive solvent and strongly dextrorotatory in acid solution.

6. Although narcotine is levorotatory in ethyl alcohol solution and dextrorotatory in acid solution, an acid alcohol solution is much more dextrorotatory than the solution of narcotine in acid alone.

The author's work is admittedly only introductory, but circumstances do not allow a further prosecution of work along these lines at present. It is in the hope that others may be attracted to an interesting field of research, that these results have been published.

XLVI.—*Studies in the Anthracene Series. Part IV.*

By EDWARD DE BARRY BARNETT and MARCUS AURELIUS
MATTHEWS.

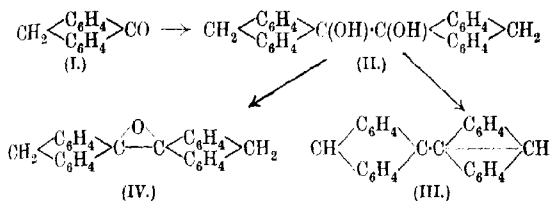
ACCORDING to Liebermann and Gimbel (*Ber.*, 1887, **20**, 1854), the reduction of anthraquinone in glacial acetic acid suspension by tin and hydrochloric acid leads either to anthrone (compare also K. Meyer, *Annalen*, 1911, **379**, 55) or dianthranyl* according to the experimental conditions used. At a later date, Eckert and Hofmann (*Monatsh.*, 1915, **36**, 497) repeated the work of Liebermann and Gimbel, but appear to have failed to obtain dianthranyl. They state, however, that dianthranyl is easily obtained by modifying the experimental conditions and give details of the preparation in which anthraquinone, suspended in boiling glacial acetic acid, is reduced by tin and hydrochloric acid in the presence of a trace of a platinum salt. We may say at once that we have repeatedly attempted to obtain dianthranyl according to these directions, but in every case have found that the sole product of the reduction is anthrone. Only in one experiment, in which the reduction was prolonged for several hours beyond the period specified by Eckert and Hofmann and in which it was carried out in a current of oxygen, was any dianthranyl isolated, and the yield in this case was very small. Neither have we been able to obtain dianthranyl by following the directions of Liebermann and Gimbel, although, judging by the fluorescence of the solutions obtained, it would seem that dianthranyl is produced in very small amount.

In view of the difficulty experienced in obtaining dianthranyl from anthraquinone by reduction with tin and hydrochloric acid a series of experiments was initiated in order to ascertain if it could be obtained by means of a different reducing agent, and at the same time an examination was also made of the behaviour of dianthrone on reduction. The present communication contains an account of this work, together with some account of the properties of dianthrone.

Anthrone (I) is very stable towards reduction with tin and hydrochloric acid in glacial acetic acid solution, with or without the addition of platinum, and is scarcely changed even after eight hours' treatment under these conditions. On the other hand, it is

* In the literature the name "dianthryl" is usually given to this compound, but as the two anthracene ring systems are joined through the *meso*-carbon atoms the correct name is "dianthranyl" (Beilstein: "Handbuch der organischen Chemie," 4th Ed., Vol. 1, p. 942).

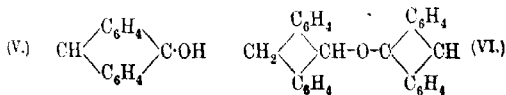
readily reduced by zinc and hydrochloric acid and then undergoes the pinacol condensation. The resulting pinacol (II), however, cannot be isolated, as it loses water in two directions, giving dianthranyl (III) and the α -pinacolin (IV) :



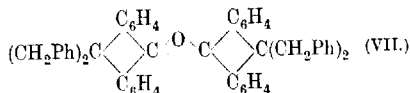
Schulze (*Ber.*, 1885, **18**, 3034), who isolated the pinacol by reducing anthraquinone with zinc dust and ammonia, stated that it passed into dianthranyl by loss of water when heated with acetyl chloride. He, however, only established the formula of the pinacol by taking the mean of three analyses in which the values for carbon and hydrogen varied between 85.79 and 86.86 per cent. and 5.56 and 6.23 per cent., respectively, and hence his results can scarcely be accepted.

The α -pinacolin is easily separated from the dianthranyl by taking advantage of the different solubilities of the two compounds in toluene. On prolonged boiling with hydrochloric acid in acetic acid solution, the ethylene-oxide ring appears to open with the formation of the pinacol (II) which, however, at once loses water and passes almost quantitatively into dianthranyl. Hence if the reduction of anthrone with zinc and hydrochloric acid is sufficiently prolonged (about eight hours), the sole product obtained is dianthranyl, the yield of the recrystallised product being upwards of 90 per cent. of that theoretically possible. This production of dianthranyl, together with the refusal of the compound to form either an acetate or a benzoate, supplies the necessary proof of the ethylene oxide structure.

In view of the ease with which anthrone (I) passes by tautomeric change into anthranol (V), it seemed possible that a somewhat similar change of the three-carbon type might take place in the case of the α -pinacolin (IV), simultaneous rupture of the ethylene-oxide ring leading to an ether (VI),



The fact that the α -pinacolin is strongly fluorescent although it contains no "bridge" bond favoured this view, but no experimental proof of the existence of the ether has as yet been obtained. In view of the marked fluorescence of the α -pinacolin it was deemed advisable to study the behaviour on reduction of some anthrone derivative in which no labile hydrogen atom was present. Dibenzylanthrone was selected for this purpose, as it is readily obtained by condensing benzyl chloride with anthrone (Hallgarten, *Ber.*, 1888, **21**, 2508). It was found to be much more resistant than anthrone to reduction with zinc and hydrochloric acid, but by substituting zinc dust for the granulated metal it is readily converted into an α -pinacolin derivative (VII), although the corresponding diphenylanthrone on reduction with zinc and acetic acid gives only diphenyldihydroanthracene (Liebermann and Lindenbaum, *Ber.*, 1905, **38**, 1803).

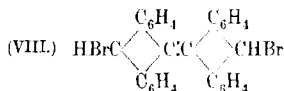


This α -pinacolin was also found to be strongly fluorescent, although there is no possibility of the presence of a "bridge" bond. Since neither anthrone nor dibenzylanthrone shows any fluorescence, the fluorescence of these α -pinacolins must be derived from the ethylene oxide part of the molecule, and may be connected with the presence of the two spirocyclic carbon atoms. In connexion with the reduction of dibenzylanthrone, it is perhaps worth noting that the reaction is accompanied by the production of a very transient orange colour. According to Meerwein (*Annalen*, 1913, **396**, 214), the pinacolin change is always preceded by the loss of water and the momentary formation of a free radicle, and if this view is correct the transient orange colour may be due to the change from the free radicle to the α -pinacolin being rather slower than is usually the case.

It is remarkable that dianthranyl had previously been prepared by several investigators, reference to whose work has been made in the foregoing, and that they all give its melting point as 300°. The present investigation, however, has shown that this figure is much too low, as the properly purified hydrocarbon does not melt at 360°. The substance described in the literature must therefore be an impure mixture, and this view is supported by statements made by previous investigators with regard to it. Thus Liebermann and Gimfel (*loc. cit.*) state that their dianthranyl, when treated with exactly two molecules of bromine in cold carbon

disulphide solution, gives chiefly dibromodianthranyl together with some dibromoanthracene. Although, as is shown in the sequel, the dianthranyl ring system is unstable under some conditions and tends to break down, it is improbable that this change would take place under the experimental conditions specified, and it is much more probable that the dibromoanthracene obtained by Liebermann and Gimbel originated with anthracene present as an impurity in the dianthranyl, more especially as Liebermann and Gimbel themselves state that their method of preparing dianthranyl leads to the simultaneous production of considerable amounts of anthracene. Further, Gimbel (*Ber.*, 1885, **18**, 2433) states that the analysis of dianthranyl derivatives is very difficult and almost always leads to low values for carbon and nitrogen. It is probable that these low values are to be attributed rather to the great difficulty of obtaining the compounds pure than to any inherent difficulty in the analytical operations. Finally, all previous investigators have described dianthranyl as being yellow, whereas when purified by our method it is quite colourless. It is also remarkable that although all previous investigators have purified their product by recrystallisation from toluene, none of them appears to have observed that dianthranyl separates from this solvent with toluene of crystallisation, although the crumbling of the crystals on drying is very noticeable.

As is well known, the "bridge" bond in the anthracene ring system acts almost exactly like a double bond in many respects. If it be regarded as equivalent to a double bond, then the *meso*-carbon atoms in dianthranyl form a conjugated system and bromine might be expected to add on to the extreme ends of the system, giving a dibromide (VIII) which would not lose hydrogen bromide :

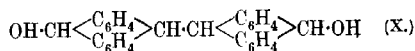
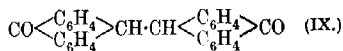


Experiment has shown, however, that when dianthranyl is treated with exactly one molecular proportion of bromine torrents of hydrogen bromide are at once evolved and a mixture of dibromodianthranyl and unchanged dianthranyl is formed.

The greater resistance shown by anthrone to reduction with tin and hydrochloric acid as compared with zinc and hydrochloric acid led us to compare the behaviour of anthraquinone under similar conditions. Liebermann and Gimbel (*loc. cit.*) and K. Meyer (*loc. cit.*) have described the preparation of anthrone by reducing anthraquinone, suspended in glacial acetic acid, with tin and

hydrochloric acid, and we have prepared considerable amounts of anthrone by this method and have found that the reaction proceeds rapidly and smoothly. If, on the other hand, zinc is substituted for tin, reduction only takes place very slowly. Anthrone seems to be formed as an intermediate product, but is then rapidly reduced, so that when the whole of the anthraquinone has disappeared almost the sole product obtained is dianthranyl.

The reduction of dianthrone (IX) by tin and hydrochloric acid in the presence of a small amount of a platinum salt has been described by Eckert and Hofmann (*loc. cit.*), who state that they obtained a compound which melted at 150–153°. This they regarded as tetrahydrodianthranyl (X) and quote analyses in agreement (Found : C = 85.8; H = 5.86 per cent.).



They further state that when the compound is heated alone or with acetic anhydride it loses water and gives dianthranyl. We have repeated their experiments and find that the reduction of dianthrone certainly leads to a compound melting at 154°, but this compound does not pass into dianthranyl by loss of water. Further, it is easily soluble in boiling dilute sodium hydroxide solution, and we have fully identified it as anthrone by direct comparison with a sample of anthrone obtained from another source, and by the preparation of anthranyl acetate and benzoate and of dibenzylanthrone, and the comparison of all these with samples of the same substances made from anthrone prepared by a different method. It is rather difficult to understand the mistake in identification made by Eckert and Hofmann, as there is an appreciable difference in the percentage composition of anthrone and tetrahydrodianthranyl ($\text{C}_{14}\text{H}_{10}\text{O}$ requires C = 86.6; H = 5.15 per cent. $\text{C}_{28}\text{H}_{22}\text{O}_2$ requires C = 86.1; H = 5.64 per cent.).

The production of anthrone by reducing dianthrone is a very remarkable reaction, for, as will be seen from the formulae, both carbonyl groups remain unaltered while rupture of a bond between two carbon atoms takes place. The reaction is all the more curious when it is remembered that dianthrone is a very stable compound and can be recrystallised unchanged from boiling concentrated nitric acid. Also the tendency to form dianthrone from anthrone or anthranol is very great. Thus Dimroth (*Ber.*, 1901, **34**, 222) obtained it in quantitative yield by oxidising anthranol with

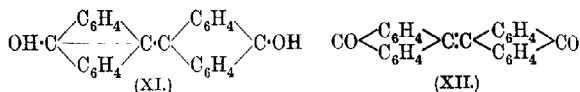
ferric chloride, and Padova obtained it by treating anthranol with phenanthraquinone (*Compt. rend.*, 1909, **149**, 217) or sulphur (*ibid.*, 1908, **148**, 292). We have also obtained it as the sole product when attempting to condense triphenylcarbinol with anthrone in the presence of zinc chloride.

The great ease with which anthrone is formed from dianthrone by reduction shows, however, that the dianthranyl ring system must become unstable under certain conditions. Further examples of this instability are to be found in the literature, as Sachse (*Ber.*, 1888, **21**, 1183) has found that dianthranyl, by treatment with chlorine or bromine, gives dichloro-(or bromo-)anthracene dichloride (or dibromide), although, as previously pointed out, these results are possibly to be attributed to anthracene present as an impurity in the dianthranyl used. More definite evidence lies in the production of dihydroanthracene by the reduction of dianthranyl by hydriodic acid and red phosphorus at 200°, and the easy and complete conversion of tetrahydrodianthranyl into dibromoanthracene by the action of bromine in carbon disulphide solution (Sachse, *Ber.*, 1888, **21**, 2512).

If the single bond which joins the two anthracene ring systems in dianthrone shows certain lack of stability, the corresponding double bond in dianthraquinone (XII) should be even less stable. The change in colour from yellow to green on warming solutions of dianthraquinone may be due to a tendency of the double bond to rupture with the formation either of a free radicle containing two carbon atoms in the tervalent state, or, more probably, of a substance in which the two free valencies only partly satisfy one another (compare Scholl, *Ber.*, 1921, **54**, [B], 2376). The fact that dianthraquinone can be recrystallised unchanged from fuming nitric acid is against this view, but some evidence has been obtained which points to a tendency of dianthranyl derivatives to dissociate. We are endeavouring to obtain more definite proof of this and therefore reserve further discussion for a future communication.

Since dianthrone is easily obtained from anthracene by treating it with nitric acid in acetic acid (Dimroth, *loc. cit.*), the reactions described above provide a ready means of preparing both anthrone and dianthranyl, the former being conveniently obtained directly from anthracene without isolating any intermediate product. Details of these preparations will be found in the experimental part of this communication, but it may here be remarked that this method of preparing anthrone is more convenient and more economical than the method previously described by one of us (Barnett and Cook, *T.*, 1921, **119**, 906) in which dihydroanthraquinyl dipyrindinium dibromide is prepared as an intermediate stage.

The enolisation of dianthrone (IX) to dianthranol (XI) takes place much less readily than the corresponding change of anthrone (I) to anthranol (V).



Thus anthrone dissolves easily in hot dilute solutions of alkali hydroxides, whereas dianthrone only dissolves in alcoholic solutions, or in aqueous solutions when heated under pressure. K. Meyer and Sander (*Annalen*, 1913, **396**, 140) have shown that anthrone is almost completely enolised in pyridine solution, and indeed in many cases pyridine seems to favour the enolisation of ketonic compounds. Thus Claisen (*Annalen*, 1896, **291**, 106; 1897, **297**, 2; *Ber.*, 1900, **33**, 1243) has shown that ethyl acetoacetate and other similar compounds give *O*-acyl derivatives on treatment with acid chlorides in the presence of pyridine, and other examples could be cited. It therefore seemed probable that dianthrone would be enolised by this reagent, and experiment has fully justified this view, enolisation being practically complete after boiling for two hours. Since dianthranol (XI) is easily oxidised to dianthraquinone (XII), this reaction has rendered the preparation of this interesting compound easy. The oxidation can be effected by ferric chloride, potassium permanganate, or potassium hypoiodite (H. Meyer, *Monatsh.*, 1909, **30**, 174; D. R.-P. 223,210), or by potassium persulphate or hydrogen peroxide (H. Meyer, Bondy, and Eckert, *ibid.*, 1912, **33**, 1447), but we have found that in the laboratory it is more convenient to effect the oxidation by adding bromine to the cold suspension of dianthranol in pyridine. Under these conditions, the dianthraquinone is obtained as an additive compound with pyridine, but this is easily decomposed by acid.

Padova (*Compt. rend.*, 1909, **148**, 290) has stated that dianthraquinone is also obtained when dianthranol is oxidised in pyridine solution with amyl nitrite. He gives no experimental details and his statement has been contradicted by H. Meyer, Bondy, and Eckert (*loc. cit.*), who claim to have proved that the product obtained by Padova was nothing but a mixture of anthraquinone and unchanged dianthranol. We have examined the reaction and find that Padova's claim is correct and that dianthraquinone is easily obtained when a boiling pyridine solution of dianthranol is treated with amyl nitrite. Nitrogenous products, however, are formed at the same time and these are at present under investigation. Padova's description of the properties of dianthraquinone is quite erroneous.

EXPERIMENTAL.

Dianthrone.—The preparation of dianthrone by the action of nitric acid on anthracene has previously been described by Dimroth (*loc. cit.*), who, however, gives very scanty details of the preparation. We have found the following method to give very satisfactory results.

One hundred grams of technical refined anthracene (about 95 per cent.) is powdered as finely as possible and suspended in 400 c.c. of glacial acetic acid. Thirty-five c.c. of concentrated nitric acid (*d* 1.420) are then run in fairly rapidly, the whole being well shaken. The anthracene slowly dissolves and the temperature rises to about 30°, but unless it tends to rise above this point cooling is not necessary. After keeping for about forty minutes with occasional shaking, the solution is filtered from a little undissolved anthracene, and the clear filtrate heated on the water-bath under reflux for one to one and a half hours. Torrents of nitric oxide are evolved and dianthrone crystallises out from the hot liquid. Without cooling, this is collected and washed with a little glacial acetic acid. The yield is about 60 grams and the substance is almost pure. By boiling the filtrate for a few minutes under reflux and then cooling, a further amount (25–30 grams) is obtained, but this is always less pure and contaminated with anthraquinone.

In the majority of our experiments we employed a particularly fine sample of commercial anthracene which was obtained from the South Metropolitan Gas Co., and the crude dianthrone then formed glistening, yellow crystals which gave a negative result when tested for anthraquinone by the usual anthraquinol test. When samples of commercial anthracene obtained from other sources were employed, it was found that the dianthrone was always contaminated with anthraquinone. The separation of these two compounds is easily effected by taking advantage of the fact that dianthrone is unaffected by boiling with zinc dust and dilute sodium hydroxide, whereas, as is well known, anthraquinone is reduced to anthraquinol, which dissolves in the alkali. The impure crude dianthrone was therefore repeatedly boiled with zinc dust and large volumes of dilute sodium hydroxide until such treatment no longer produced a red solution. After washing, excess of zinc dust was removed by digestion with dilute hydrochloric acid, and the dianthrone finally well washed and dried in the oven. Thus obtained, it formed a yellow, sandy powder which is quite pure enough for most purposes.

Dianthranol.—Ten grams of dianthrone were boiled under reflux with 75 c.c. of pyridine for two hours. On cooling the resulting dark-coloured solution, dianthranol separated in fine leaflets,

which were very difficult to filter. It was identified by its easy oxidation to dianthraquinone, by its solubility in alkali hydroxide solutions, and by the preparation of the diacetate and dibenzoate.

Dianthranol Diacetate.—Five grams of dianthrone were enolised by boiling with pyridine as described above. The solution was then cooled as rapidly as possible and the resulting suspension of dianthranol treated with 7 c.c. of acetic anhydride. The dianthranol dissolved almost at once and after heating on the water-bath for thirty minutes the whole was kept at the ordinary temperature over-night. The yellow crystals were then collected and twice recrystallised from glacial acetic acid. This acetate has previously been prepared by H. Meyer (*Monatsh.*, 1909, **30**, 165) by heating dianthranol with acetic anhydride and sodium acetate, and he gives the melting point as 273–275°. Eckert and Hofmann (*ibid.*, 1915, **36**, 501), who obtained it by oxidising dianthranol with lead dioxide in glacial acetic acid solution, give the melting point as 284°. Our sample melted at this latter point after darkening and sintering at about 275°. The melting point was not changed by further recrystallisation from either glacial acetic acid or alcohol.

Dianthranol Dibenzoate.—Benzoyl chloride (10 c.c.) was added drop by drop to a cold suspension of dianthranol in pyridine, obtained as described above from 10 grams of dianthrone. The dianthranol dissolved, and on keeping over-night at the ordinary temperature a yellow precipitate separated. This was collected and washed first with pyridine and then with ether. It was then thoroughly triturated with cold sodium carbonate solution, washed with a large volume of cold water, and finally dried for several days in a vacuum desiccator (Found: C = 85.0; H = 4.45. $C_{42}H_{26}O_4$ requires C = 84.9; H = 4.38 per cent.). Dianthranol dibenzoate forms a sulphur-yellow powder which darkens on exposure to light. It can be recrystallised from aqueous pyridine or a mixture of benzene and light petroleum. It does not melt below 350°.

Dianthraquinone.—(a) Ten grams of dianthrone were enolised by boiling with 75 c.c. of pyridine as described above. The cold suspension of dianthranol was then treated slowly with a solution of 4.2 grams of bromine in 25 c.c. of pyridine. The addition of each drop of the bromine solution produced an intense green colour, but this vanished rapidly on shaking. After the bromine had been added, the whole was kept at the ordinary temperature for an hour, and the crystals then collected and washed first with pyridine and then with ether. The product thus obtained is well-crystallised and appears to be an additive compound of dianthraquinone and pyridine, as it contains nitrogen but no bromine and

does not become green on rubbing. Owing to its instability, it could not be purified for analysis. The pyridine is lost on washing with water, but the dianthraquinone is then obtained in a very finely divided state and is almost impossible to filter. The best method of decomposing the additive compound is to add it little by little to boiling dilute hydrochloric acid. The yield of dianthraquinone is about 7 grams, and by pouring the pyridine liquors into a large volume of dilute hydrochloric acid a further 2.5 grams of rather less pure material can be obtained. It can be recrystallised from boiling xylene, in which, however, it is but sparingly soluble.

(b) Ten grams of dianthrone were enolised by boiling with pyridine as described above, and to the still boiling solution 10 c.c. of amyl nitrite were added fairly rapidly from a dropping funnel. The whole was boiled vigorously for a further period of fifteen minutes and the green solution then cooled. The dianthraquinone was collected and purified as described above.

Reduction of Dianthrone. Preparation of Anthrone.—One hundred grams of dianthrone, 75 grams of granulated tin, 500 c.c. of glacial acetic acid, and a few drops of a dilute solution of platinum chloride were boiled under reflux, and 50 c.c. of fuming hydrochloric acid slowly added. The whole of the dianthrone dissolved in about forty minutes and the boiling was continued for a further period of twenty minutes, and the hot solution then filtered. After cooling, the anthrone was collected and washed first with glacial acetic acid, then with hot dilute hydrochloric acid, and finally with water. The yield was 77 grams, and a further 15 grams of rather less pure material were obtained by diluting the acetic acid liquors. After drying in a vacuum desiccator, the sample melted at 154°; alone or mixed with anthrone obtained from another source. In order to complete the identification, part of the anthrone was converted into anthranol acetate and benzoate, and these were identified by the method of mixed melting points. The acetate was made by dissolving 5 grams of anthrone in 35 c.c. of pyridine and then adding 5 c.c. of acetic anhydride. After heating on the water-bath in a current of carbon dioxide for two hours, the solution was diluted with water and cooled. The precipitate was collected, washed, and twice recrystallised from alcohol. It then sintered at 128° and melted at 132–134°. This is a more convenient method of preparation than that described by Liebermann and Topf (*Annalen*, 1882, **212**, 8; *Ber.*, 1876, **9**, 1202), who heated anthrone with acetic anhydride at 160–170° in a sealed tube. They give the melting point of the acetate as 126–131°.

The benzoate was prepared in pyridine solution by means of benzoyl chloride (5 grams of anthrone, 35 c.c. of pyridine, and

5 c.c. of benzoyl chloride), but the solution was only warmed very gently for ten minutes. It is best purified by recrystallisation from a mixture of one volume of pyridine and three volumes of alcohol, and then melts at $170-172^{\circ}$. Padova (*Compt. rend.*, 1906, **143**, 121), who prepared it by boiling anthranol with benzoyl chloride in pyridine solution, gives the melting point as $163-165^{\circ}$.

In the above preparation of anthrone, granulated zinc can be substituted for the tin, but if this is done it is essential to stop the reaction as soon as the dianthrone has dissolved, as otherwise the reaction will go too far.

For the preparation of anthrone, it is quite unnecessary to isolate the dianthrone, and excellent results are obtained if anthracene (20 parts) is dissolved in acetic and nitric acids as described on page 387 and the filtered solution then heated first on the water-bath and then to boiling under reflux until no more gas is evolved. The nitric oxide is then removed by a current of carbon dioxide, and, without cooling, granulated tin (10 parts) and a few drops of a platinum chloride solution are added. The reduction is then carried out as described above. The yield of anthrone is 17 parts, and further amounts can be obtained by concentrating or diluting the liquors. The anthrone thus obtained is slightly yellow in colour, but is quite pure enough for almost all purposes.

Reduction of Anthrone. Preparation of Dianthranyl.—(a) Twenty-five grams of anthrone and 15 grams of granulated zinc were boiled under reflux with 125 c.c. of glacial acetic acid, and 15 c.c. of fuming hydrochloric acid added drop by drop. After about fifteen minutes, glistening crystals began to separate from the boiling solution, and at the end of a further hour the solution had become pasty. The reaction was then stopped, and after cooling, the crystals were collected and washed with glacial acetic acid, dilute hydrochloric acid, and water. The product was dried in the steam-oven and then dissolved in boiling toluene. The filtered solution, on cooling, deposited glistening, yellow crystals of the toluene additive compound of dianthranyl, but these lost their toluene and fell to a powder on drying in the steam-oven. The yield was 9 grams. For analysis, it was recrystallised three times from pyridine and then once from carbon tetrachloride and once from benzene. It then formed a snow-white, crystalline powder which did not melt at 360° (Found: C = 94.5; H = 5.31; *M* (naphthalene solution) = 342. Calc., C = 94.9; H = 5.09 per cent.; *M* = 354). The purification by means of carbon tetrachloride and benzene is very troublesome owing to the slight solubility of dianthranyl in these solvents, but unless these solvents were used it was found impossible to obtain a pure substance.

The toluene liquors from which the dianthranyl had separated were concentrated by distillation and finally taken to dryness on the water-bath in a vacuum. The residue was thoroughly washed with ether and recrystallised from a mixture of methyl ethyl ketone and alcohol, and then formed an almost colourless, crystalline powder. The yield was 9 grams. For analysis, it was recrystallised successively from a mixture of chloroform and light petroleum, pyridine and water, pyridine and absolute alcohol, and finally from a mixture of benzene and ether. It then melted sharply at 219° and the melting point was not changed by several subsequent crystallisations from various solvents (Found: C = 90.0; H = 5.47. $C_{28}H_{20}O$ requires C = 90.3; H = 5.38 per cent.).

α -Anthrapiocolin (Ethylene Oxide dispiro-9 : 10 : 9' : 10'-Dihydro-anthracene) (Formula IV) is almost insoluble in alcohol, ether, acetone, or light petroleum, but easily soluble in most other media. Its solutions, especially those in the aromatic hydrocarbons, exhibit a violet fluorescence which is redder and less strongly marked than that shown by dianthranyl. It gives an acetyl derivative neither when heated with pyridine and acetic anhydride nor when boiled with acetic anhydride and sodium acetate under reflux. Two grams, when boiled under reflux for eight hours with 50 c.c. of glacial acetic acid with the slow addition of 15 c.c. of fuming hydrochloric acid, passed into dianthranyl, the yield of the recrystallised hydrocarbon being 1.4 grams.

(b) Twenty grams of anthrone, 20 grams of granulated zinc, and 100 c.c. of glacial acetic acid were boiled under reflux for eight hours, 40 c.c. of fuming hydrochloric acid being added slowly during the first five hours. After cooling, the precipitate was collected, washed, dried, and recrystallised from toluene. The yield of dianthranyl was 16 grams, and on evaporating the toluene liquors to dryness no α -pinacolin was found. This is the best method of preparing dianthranyl, as although it can be obtained directly from anthracene without isolating the anthrone the method is not satisfactory.

Reduction of Dibenzylanthrone.—Dibenzylanthrone was prepared from anthrone and benzyl chloride according to the directions given by Hallgarten (*loc. cit.*). The yield of the crude product was 29 grams from 40 grams of anthrone. It was purified by recrystallisation first from aqueous pyridine and then from a mixture of benzene and light petroleum. The purified product melted at 227° , and the melting point was not changed by further recrystallisation from a mixture of chloroform and light petroleum. The melting point given by Hallgarten, 217° , is therefore too low.

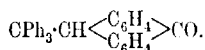
Ten grams of pure dibenzyl anthrone were boiled under reflux

with 50 c.c. of glacial acetic acid. To the boiling solution 5 grams of zinc dust were added in three portions, and 5 c.c. of fuming hydrochloric acid dropped in slowly. The addition of each drop of acid gave rise to a transient orange colour. At the end of three hours the reaction was stopped, and after cooling, the precipitate was collected, washed with dilute hydrochloric acid and water, and dried in a vacuum desiccator. The crude product was thoroughly washed with ether, which removed substances having low melting points, and then extracted with boiling benzene so long as the extracts showed a strong fluorescence. The united extracts were diluted with light petroleum, and the resulting almost colourless precipitate was dissolved in boiling pyridine and boiled with animal charcoal for an hour. The clear filtrate was diluted with alcohol and then a little water added. On cooling, a colourless, indistinctly crystalline powder separated which sintered at 235° and melted indefinitely at 260—270°. It was analysed in this state, and was then recrystallised from a mixture of toluene and light petroleum and again analysed, although the melting point had not altered (Found: C = 92.0, 92.1; H = 6.10, 6.16. $C_{36}H_{44}O$ requires C = 91.8; H = 6.01 per cent.).

Tetrabenzyl- α -anthrapinacolin (formula VII) is very easily soluble in most media, but is almost insoluble in ether or light petroleum. Its solutions exhibit a vivid blue fluorescence.

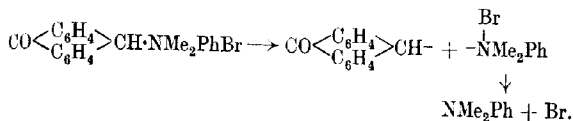
[With RONALD FRANCIS HURT.]

Khotinsky and Patzewitch (*Ber.*, 1909, **42**, 3104) have shown that triphenylcarbinol condenses easily with pyrrole under the influence of zinc chloride and gives an almost quantitative yield of triphenylpyrrylmethane. In view of the reactive nature of the *meso*-hydrogen atoms in anthrone, it seemed possible that a similar condensation might take place between this compound and triphenylcarbinol, with the formation of triphenylmethylanthrone,



Such a compound would be of considerable interest as it, or its enolic isomeride, would tend to dissociate into free radicals. Attempts were therefore made to condense triphenylcarbinol with anthrone, but the sole product obtained was dianthrone. It would therefore appear that triphenylcarbinol acts as an oxidising agent. This seems scarcely likely, and a more reasonable explanation is that triphenylmethylanthrone is actually first formed and then dissociates into triphenylmethyl and an anthronyl radicle, two of these latter subsequently uniting to form dianthrone. It may be

pointed out that a similar reaction may possibly account for the abnormal production of dianthrone and free bromine when bromo-anthrone is treated with certain amines (Barnett, Cook, and Grainger, T., 1922, 121, 2063). In these cases, a quaternary salt is probably first formed, which then dissociates into free radicals. The reaction is simplest in the case of dimethylaniline, and in this case can be represented as follows :



This explanation is put forward with some reserve, pending a more detailed examination of the reaction. As one of us (R. F. H.) is unable to continue the work, it is thought best to publish this short note and reserve a fuller discussion for a future occasion.

Ten grams of anthrone, 13 grams of triphenylcarbinol, and about 10 grams of zinc chloride were boiled under reflux with 400 c.c. of glacial acetic acid for eight hours, a current of carbon dioxide being passed during the whole time to prevent oxidation by atmospheric oxygen. After cooling, the precipitate was collected and recrystallised several times from a mixture of chloroform and light petroleum. The resulting colourless crystals were identified as dianthrone by direct comparison with a sample of the substance from a different source, by the usual colour reactions and by a quantitative oxidation to anthraquinone (Found : anthraquinone = 107.1. Calc., 107.8 per cent.).

Summary.

(i) Anthrone is very stable towards reduction with tin and hydrochloric acid, but is easily reduced by zinc and hydrochloric acid, and then gives a mixture of α -anthrapinacolin and dianthranyl, the former passing into the latter on further treatment with hydrochloric acid.

(ii) Dianthrone on reduction with hydrochloric acid and either tin or zinc passes into anthrone.

(iii) Dianthrone is almost completely enolised to dianthranol by boiling with pyridine.

(iv) Convenient methods for the preparation of anthrone (direct from anthracene), dianthrone, dianthranol, dianthraquinone, and dianthranyl have been worked out.

(v) Some evidence has been accumulated which points to a tendency on the part of the *meso*-carbon atoms of the anthracene ring system to act in the tervalent state.

In conclusion, the authors desire to express their thanks to the South Metropolitan Gas Co. for gifts of anthracene and pyridine, and to the Research Fund Committee of the Chemical Society for a grant which has partly defrayed the expense of this research.

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[Received, December 29th, 1922.]

XLVII.—*Derivatives of Semioxamazide. Part I.* *Ketonic Semioxamazones.*

By FORSYTH JAMES WILSON and ERIC CHARLES PICKERING.

SEMIOXAMAZIDE, $\text{NH}_2\cdot\text{NH}\cdot\text{CO}\cdot\text{CO}\cdot\text{NH}_2$, prepared by Kerp and Unger (*Ber.*, 1897, **30**, 585), was found to react readily with aldehydes, giving semioxamazones of the type $\text{CHR:N}\cdot\text{NH}\cdot\text{CO}\cdot\text{CO}\cdot\text{NH}_2$; it reacted much less readily, however, with ketones. A further investigation was carried out by Radcliffe and Loo (*Perf. and Essent. Oil Rec.*, 1919, **10**, 39), who also found that the reaction was a general one for aldehydes, but that the application to ketones was limited; no acetone derivative, for example, could be obtained, as had been already noted by Kerp and Unger.

We have found that the reaction between semioxamazide and ketones is far more general than the literature indicates, and have worked out what appears to be a general method for the preparation of such ketonic derivatives. The semioxamazones of the lower aliphatic ketones are very easily hydrolysed by water alone, so that dry solvents should be employed; in this way, the acetone derivative can be easily prepared. The reaction between ketones and semioxamazide in absolute alcohol is accelerated to a remarkable extent by the addition of a small quantity of iodine (see experimental part).

The method we have adopted is to heat on the water-bath the calculated quantities of ketone and finely powdered semioxamazide in absolute alcohol. A small quantity of iodine is added to the boiling liquid, the semioxamazide, which is insoluble in alcohol, rapidly dissolves, and the semioxamazone separates on cooling. In the case of unsaturated ketones, we have avoided the use of iodine, and have simply heated the ketone and semioxamazide in absolute alcohol until solution is complete. The use of iodine in anil formation is referred to by Knoevenagel (*J. pr. Chem.*, 1914, [ii], **89**, 37).

We have prepared the semioxamazones of the following ketones

—acetone, methyl ethyl ketone, methyl isopropyl ketone, methyl isobutyl ketone, mesityl oxide, acetophenone, benzylacetone, styryl methyl ketone, and phenyl *p*-tolyl ketone. With the exception of the semioxamazones of acetophenone and styryl methyl ketone, which have been already prepared by Kerp and Unger and by Radcliffe and Loo, respectively (*loc. cit.*), these derivatives do not appear to have been previously described. Styryl methyl ketone semioxamazone is markedly phototropic, rapidly changing from white to yellow on exposure to light.

The ketonic semioxamazones give monosodium and monopotassium derivatives which are very readily decomposed by moisture; these are described in the experimental part. They are presumably derived from the semioxamazone by the replacement of the imino-hydrogen by metal. We have also prepared a monosodium derivative of semioxamazide itself.

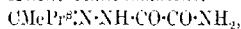
We propose to continue the investigation of these semioxamazones and their metallic derivatives, and also to study the action of iodine in similar reactions.

EXPERIMENTAL.

Acetonesemioxamazone, $\text{CMe}_2\text{N}\cdot\text{NH}\cdot\text{CO}\cdot\text{CO}\cdot\text{NH}_2$.—Five grams of dry semioxamazide were heated with 30 c.c. of dry acetone on the water-bath for one hour, when the semioxamazide had completely dissolved; in presence of a little iodine, three minutes were sufficient. The product which separated on cooling crystallised from acetone in long, white needles melting at 147° (Found: $\text{N} = 29.5$. $\text{C}_5\text{H}_9\text{O}_2\text{N}_3$ requires $\text{N} = 29.4$ per cent.). The same substance was obtained by heating the calculated quantities of dry semioxamazide and dry acetone in absolute alcohol for forty minutes, or for two minutes in presence of a little iodine, and separated on cooling.

Methyl Ethyl Ketone Semioxamazone, $\text{CMeEtN}\cdot\text{NH}\cdot\text{CO}\cdot\text{CO}\cdot\text{NH}_2$, was prepared by the same methods as the acetone derivative, in the first method forty-five minutes being required without iodine and one minute with iodine, and in the second method, ninety minutes without iodine and three minutes with iodine. The substance was recrystallised from absolute alcohol, from which it separated in small, colourless needles melting at 127° (Found: $\text{N} = 26.8$. $\text{C}_8\text{H}_{11}\text{O}_2\text{N}_3$ requires $\text{N} = 26.7$ per cent.). Like acetonesemioxamazone, it is hydrolysed on warming with moist ether or dilute alcohol.

Methyl isoPropyl Ketone Semioxamazone.



was prepared as in the previous cases; heating in absolute alcohol required seventy minutes without iodine and ten minutes with iodine. Recrystallisation from absolute alcohol gave colourless

needles melting at 143° (Found: $N = 24.7$. $C_7H_{13}O_2N_3$ requires $N = 24.5$ per cent.).

Methyl isobutyl Ketone Semioxamazone,



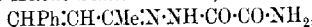
—This semioxamazone is apparently not hydrolysed by water and was obtained by heating a concentrated aqueous solution of semioxamazine with the calculated quantity of the ketone in alcoholic solution for about half an hour, a method which was quite ineffective in the previous cases. The substance separated from the reaction mixture, on cooling, in colourless needles which, after recrystallisation from alcohol, melted at 133° (Found: $N = 22.9$. $C_8H_{15}O_2N_3$ requires $N = 22.7$ per cent.).

Mesityl Oxide Semioxamazone, $CMe_2 \cdot CH \cdot CMe \cdot N \cdot NH \cdot CO \cdot CO \cdot NH_2$, was prepared in the same way as methyl isobutyl ketone semioxamazone, one hour's heating being necessary, or by heating the ketone in absolute alcohol with semioxamazine. On cooling, the semioxamazone slowly separated as a white powder, which was obtained in colourless plates, melting at 163 – 164° after recrystallisation from alcohol (Found: $N = 23.0$. $C_8H_{13}O_2N_3$ requires $N = 22.9$ per cent.).

Acetophenonesemioxamazone, $CPhMe \cdot N \cdot NH \cdot CO \cdot CO \cdot NH_2$, has already been described by Kerp and Unger and by Radcliffe and Loo (*loc. cit.*). We have prepared it by heating the ketone with semioxamazine in absolute alcohol without iodine (one hour) or with iodine (five minutes).

Benzylacetonesemioxamazone, $CH_2Ph \cdot CH_2 \cdot CMe \cdot N \cdot NH \cdot CO \cdot CO \cdot NH_2$, was obtained by heating 2 grams of the ketone and 1 gram of semioxamazine in 20 c.c. of absolute alcohol without iodine (three hours) or with iodine (four minutes). The semioxamazone, which separated on cooling, was washed with ether and recrystallised from alcohol, from which it was deposited in small, colourless needles melting at 125° (Found: $N = 18.3$, 18.1 . $C_{12}H_{15}O_2N_3$ requires $N = 18.0$ per cent.).

Styryl Methyl Ketone Semioxamazone,



was prepared by the method described by Radcliffe and Loo, who give the melting point as 211 – 212° ; we found that it melted at 220 – 221° (Found: $N = 18.1$. Calc., $N = 18.1$ per cent.). It rapidly becomes yellow on exposure to light, the melting point remaining unchanged.

Phenyl p-Tolyl Ketone Semioxamazone,



obtained by heating molecular quantities of the ketone and semioxamazine in absolute alcohol with a little iodine, formed colour-

less prisms melting at 197° after recrystallisation from alcohol (Found: $N = 15.0$. $C_{16}H_{15}O_2N_3$ requires $N = 14.9$ per cent.).

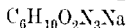
Metallic Derivatives of the Semioxamazones and of Semioxamazide.

These metallic derivatives were prepared by heating on the water-bath the semioxamazone or semioxamazide, dissolved or suspended in absolute alcohol, with sodium ethoxide (1 mol.), or potassium hydroxide, dissolved in absolute alcohol. The semioxamazone or semioxamazide, if in suspension, soon dissolved to a yellow solution, and after boiling for a short time the metallic derivative was precipitated as a powder. Sometimes the precipitation was rather slow; in such a case the alcoholic solution was cooled and then poured into a large volume of dry ether. The metallic derivative was collected, washed with absolute alcohol, in which it was sparingly soluble or insoluble, and dried in a vacuum over sulphuric acid. These metallic derivatives are colourless powders with the exception of those of styryl methyl ketone semioxamazone, which are pale yellow, and are all decomposed more or less readily by moisture. The compounds described below were prepared.

(a) *Sodium derivative of:*

Acetonesemioxamazone. Found: $Na = 13.5, 14.0$. $C_5H_8O_2N_3Na$ requires $Na = 13.9$ per cent.

Methyl ethyl ketone semioxamazone. Found: $Na = 12.1$.



requires $Na = 12.8$ per cent.

Mesityl oxide semioxamazone. Found: $Na = 10.8$. $C_8H_{12}O_2N_3Na$ requires $Na = 11.2$ per cent.

Styryl methyl ketone semioxamazone. Found: $Na = 8.8, 8.9$. $C_{12}H_{12}O_2N_3Na$ requires $Na = 9.1$ per cent.

Semioxamazide. Found: $Na = 18.0, 18.4$. $C_2H_4O_2N_3Na$ requires $Na = 18.4$ per cent.

(b) *Potassium derivative of:*

Acetophenonesemioxamazone. Found: $K = 15.9$. $C_{10}H_{10}O_2N_3K$ requires $K = 16.0$ per cent.

Styryl methyl ketone semioxamazone. Found: $K = 14.4, 14.4$. $C_{12}H_{12}O_2N_3K$ requires $K = 14.5$ per cent.

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(Received, December 28th, 1922.)

XLVIII.—*The Densities of Dilute Solutions of Potassium Salts and the Volume Changes Occurring on Solution.*

By HAROLD HARTLEY and WILLIAM HENRY BARRETT.

IN a previous communication, the authors made a critical examination of the conditions under which accurate determinations of density could be made with pyknometers of comparatively small capacity (T., 1911, 99, 1072). It was found that by using a pyknometer of about 25 c.c. capacity and a counterpoise with a volume equal to the sum of the volumes of the glass of the pyknometer and of its liquid content when filled to the mark, the density of dilute aqueous solutions could be determined without difficulty with an accuracy of 2 or 3 units in the sixth decimal place. The densities are calculated from the expression

$$d_1 = d_w \frac{W_3 - W_1 + \Delta_1 V_p}{W_2 - W_1 + \Delta_1 V_p},$$

where d_1 and d_w are the densities of solution and water, respectively (referred to water at 4° as unity); W_1 , W_2 , and W_3 are the apparent weights in air of the pyknometer empty and filled with water and solution, respectively; Δ_1 is the density of the air at the time of the weighing W_1 ; and V_p is the volume of the liquid which fills the pyknometer up to the mark.*

It is often assumed that if an accuracy approaching one part in a million is required in density determinations, pyknometers containing relatively large quantities of solution must be used, but a series of determinations of the density for dilute solutions of potassium salts at 18° has confirmed the results described in the previous paper, as duplicate determinations for the same solution agreed usually within 2 or 3 units and always within 5 or 6 units in the sixth decimal place. The presence of dissolved air introduces an uncertainty of one part in a million in the density of aqueous solutions at 18°.

The potassium salts used were Merck's purest, recrystallised from water several times, the crystals each time being drained on a porcelain centrifuge. The solutions were made up by weight. At least two or three determinations were made of the density of each solution, either with two different pyknometers or with two separate fillings of the same pyknometer. The details of the determinations are described in the previous paper. The mean

* In the previous paper (*loc. cit.*), $W_1 - \Delta_1 V_p$ should be substituted for W_1 at the head of the first column of the first table on p. 1074.

value found for the density of each solution examined is given in column IV of the following table :

Densities of Solutions at 18° and Total Contractions Occurring on Solution.

I.	II.	III.	IV.	V.		VI.
Density of solid salts.	Grams of salt in 1000 grams of water.	Gram-mol. of salt per litre of solution.	d_4^{18} of solution.	Total contraction in c.c. per gram of dissolved salt.		per gram-mol. of dissolved salt.
KCl d_4^{18} 1.986 (Baxter)	16.445	0.2189	1.008996	0.138		10.3
	4.132	0.05529	1.001316	0.157		11.7
	2.873	0.03844	1.000502	0.159		11.85
	0.9349	0.01252	0.999237	0.162		12.1
	0.6323	0.008467	0.999038	0.161		12.0
	0.4087	0.005473	0.998890	0.158		11.8
	0.2833	0.003794	0.998808	0.16 ₆		12.4
	0.1836	0.002459	0.998744	0.16 ₆		12.4
	0.0		0.998622	0.16 ₆		12.4
KBr d_4^{18} 2.751 (Baxter)	13.145	0.1099	1.007976	0.078		9.3
	8.154	0.0682	1.004474	0.083		9.9
	4.162	0.0349	1.001623	0.086		10.2
	1.888	0.0158	0.999990	0.089		10.6
	0.0			0.090		10.7
KI d_4^{18} 3.126 (Baxter)	23.077	0.1379	1.015300	0.048		7.95
	9.546	0.0573	1.005569	0.050		8.3
	7.286	0.0437	1.003940	0.052		8.6
	4.816	0.0289	1.002138	0.052		8.6
	0.0			0.053		8.8
KClO ₃ d_4^{18} 2.344 (Retgers)	18.268	0.1478	1.010042	0.056		6.9
	8.428	0.0685	1.003978	0.064		7.8
	6.102	0.0496	1.002474	0.060		7.4
	1.014	0.00826	0.999268	0.065		8.0
	0.0			0.066		8.1
KBrO ₃ d_4^{18} 3.323 (Clarke)	18.417	0.1096	1.012138	0.039		6.5
	8.766	0.0523	1.005088	0.041		6.8
	3.847	0.0230	1.001481	0.045		7.5
	2.233	0.0133	1.000282	0.046		7.7
	0.0			0.047		7.8
KIO ₃ d_4^{18} 3.979 (Kremers)	30.135	0.1399	1.023770	0.091		19.5
	12.651	0.0589	1.009268	0.095		20.3
	3.926	0.0183	1.001949	0.100		21.4
	3.280	0.0153	1.001400	0.099		21.2
	0.0			0.100		21.4
KNO ₃ d_4^{18} 2.106 (Bellatti and Finazzi)	20.097	0.1969	1.010775	0.084		8.5
	9.652	0.0950	1.004531	0.090		9.1
	6.395	0.0630	1.002546	0.090		9.1
	3.009	0.0297	1.000481	0.093		9.4
	1.549	0.0153	0.999581	0.095		9.6
	0.0			0.096		9.7

1000 Grams of water at 18° occupy 1001.380 c.c.

In dilute solutions the variation of density with concentration is nearly linear. For solutions of potassium nitrate below one-

fifth normal the densities within the limits of experimental error can be expressed by the equation

$$d_4^{20} = 0.998622 + 0.000618 c - 0.00000065 c^2,$$

where c is the concentration expressed as grams of salt in 1000 grams of water. The densities of the other solutions examined cannot be represented satisfactorily by such a simple expression.

Change of Volume on Solution.

The total change in volume which occurs during the process of solution has been calculated for each solution by subtracting from the sum of the volumes occupied by the water and salt that occupied by the solution they produce. The results are given in columns V and VI of the above table for one gram and for one gram-molecule of dissolved salt, respectively. The concordance of these values for each salt in dilute solution affords a delicate criterion of the accuracy of the density determinations, as an error of one unit in the sixth decimal place of the density affects the total volume change by approximately 1 per cent. in 0.01N-solution. The values of Baxter (*J. Amer. Chem. Soc.*, 1916, **38**, 259) for the densities of potassium chloride, bromide, and iodide were used in calculating the volume of the salt; the values taken for the remaining salts were probably less accurate, as they cannot be fused without decomposition, but an error in the density of the solid is of less importance than an error in the density of the solution, for example, in 0.01N-salt solutions an error of 0.1 per cent. in the case of the solid has the same effect on the result as an error of 0.0001 per cent. in the case of the solution.

Lamb and Lee (*J. Amer. Chem. Soc.*, 1913, **35**, 1667) have determined the change in volume when a salt is dissolved in water for dilute solutions of a few salts at 20°, and Baxter and Wallace have measured the same quantity for stronger solutions of salts over a considerable temperature range. Although an exact comparison cannot be made, the following values show that the present values are in substantial agreement with those of previous investigations, bearing in mind that the contraction decreases with rise of temperature.

Contraction per Gram of Dissolved Salt on Formation of Potassium Chloride Solutions.

Concentration in gram-mol. per litre.	Hartley and Barrett at 18°.	Baxter at 25°	Lamb and Lee at 20°.
0.1652	0.145 c.c.	0.1365 c.c.	—
0.0100	0.162	—	0.151 c.c.
0.0	0.16 ₄	—	0.153

It will be noted that the process of solution is accompanied by a contraction in each case, and the variation of the contraction is small in dilute solutions. The very accurate determinations of Lamb and Lee, who measured the density to one part in ten million, show that for salts of univalent ions the contraction does not increase more than 1 per cent. between 0.01*N* and infinite dilution. Baxter suggests that two volume changes are involved, namely, an increase in volume of the ions on being relieved from the restraint of the crystal structure and a contraction resulting from their subsequent hydration but no quantitative theory has been suggested to account for the results. The following comparison of values for the salts examined is of interest in showing that the contraction at infinite dilutions is approximately the same for each, except for potassium iodate, and amounts to a considerable proportion of the molecular volume in the solid state :

	Contraction (c.c.) on solution of 1 gram-mol. of salt at infinite dilution at 18°.	Mol. volume (c.c.) of solid salt.		Contraction (c.c.) on solution of 1 gram-mol. of salt at infinite dilution at 18°.	Mol. volume (c.c.) of solid salt.
KCl	12.3	37.5	KBrO ₃ ...	7.8	50.2
KBr ...	10.7	43.3	KIO ₃	21.4	53.7
KI	8.8	53.1	KNO ₃	9.7	48.0
KClO ₃ ...	8.1	52.2			

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[Received, January 12th, 1923.]

XLIX.—*The Estimation of Acetone in Methyl Alcohol and the Purification of Methyl Alcohol by Sodium Hypoiodite.*

By HENRY HUTCHINSON BATES, JOHN MYLNE MULLALLY, and
HAROLD HARTLEY.

ACETONE in methyl alcohol is usually estimated by the method due to Messinger (*Ber.*, 1888, **21**, 3366). Two c.c. of methyl alcohol are added to 20 c.c. of *N*-sodium hydroxide and after the addition of 20 c.c. of 0.2*N*-iodine solution the mixture is shaken for a quarter to half a minute until it is clear. It is then just acidified with *N*-hydrochloric acid, excess of 0.1*N*-sodium thiosulphate is added, and the excess titrated with 0.2*N*-iodine solution. Messinger's own results were usually low, although the alcohol he called "purissimum" gave an acetone constant of 0.06 per cent.

Goodwin (*J. Amer. Chem. Soc.*, 1920, **42**, 39) investigated this

method of estimating acetone in aqueous solutions and found that it gave accurate results, provided that the mixture is well shaken while the iodine is being added, and that sufficient time is allowed for the acetone to react with the hypoiodite. He considered twenty minutes sufficient for this purpose even in cold weather.

Both Goodwin (*loc. cit.*) and Rakshit (*Analyst*, 1916, **41**, 246) found that the method gives too high results for acetone in presence of methyl alcohol.

The following experiments were made to determine the error introduced by the reaction of the methyl alcohol with the hypoiodite. Successive quantities of 20 c.c. of methyl alcohol free from acetone were mixed with 40 c.c. of 0.5N-sodium hydroxide and 20 c.c. of 0.1N-iodine solution, and after known times the solutions were acidified and the iodine titre was determined with sodium thiosulphate. In a blank experiment without methyl alcohol, no change in the iodine titre was found after twenty-four hours, whilst the following amounts (x c.c.) of 0.1N-iodine were found to have reacted with the methyl alcohol in the times mentioned :

	Mins.				Hrs.		
Time	2	5	10	20	2.25	19	53
x	0.48	1.6	2.7	4.0	8.33	9.35	9.45

The reaction between the hypoiodite and methyl alcohol is incomplete owing to the speed at which the former substance is converted into iodate. Schwicker (*Z. physikal. Chem.*, 1895, **16**, 303) has measured the rate of the reaction



and found that at a dilution of 0.016N, in presence of excess of hydroxyl-ion, the period of half-change is twenty-five minutes at 12°.

The above experiments having shown the importance of the time factor in acetone determinations, the following standard conditions were chosen: 20 c.c. of methyl alcohol were diluted to 100 c.c. with water, 25 c.c. of this solution were then mixed with 20 c.c. of 0.5N-sodium hydroxide and 25 c.c. of 0.1N-iodine solution, and the mixture was shaken at intervals for half an hour. It was then acidified with 0.5N-sulphuric acid, and the unused iodine titrated with sodium thiosulphate. The experiments were carried out at a temperature of $15 \pm 0.5^\circ$.

In order to find the zero error under these conditions successive equal quantities of acetone-free methyl alcohol were diluted as above with water containing known quantities of acetone and the acetone was estimated as described.

The amounts (x c.c.) of 0·1*N*-iodine solution used up were as follows, a denoting the percentage of acetone added :

a	0·013	0·032	0·064	0·096	0·128	0·160
x	1·02	1·82	3·16	4·46	5·80	7·12

The results, when plotted, lie on a straight line which cuts the vertical axis at 0·5 c.c., indicating that 0·5 c.c. of iodine (corresponding with 0·012 per cent. of acetone) would be used up in pure methyl alcohol and would thus be the zero error of the estimation.

In order to test this further, acetone-free methyl alcohol was obtained from four separate sources (a) a sample purified by repeated treatment with acid mercuric sulphate solution and given to us by Dr. Whiteley, (b) a sample obtained from Hopkins and Williams, (c) and (d) specimens purified by the methyl oxalate and the hypiodite methods, respectively. The results of acetone determinations carried out as above with these samples are :

	(a).	(b).	(c).	(d).
C.c. of 0·1 <i>N</i> -iodine used	0·49	0·52	0·50	0·48

The results in each case agree within the limit of experimental error and show that under these conditions 0·012 per cent. must be subtracted from the amount of acetone found, to allow for the reaction of the hypiodite with the methyl alcohol. Repeated purification of methyl alcohol failed to give a lower apparent acetone content.

As other methods of removing acetone from methyl alcohol had been found to be inefficient or to give poor yields, Messinger's method has been adapted to this purpose. Considerable dilution with water is obviously undesirable, as methyl alcohol will be lost in rectification; on the other hand, it was found necessary to dilute to a definite extent and also to use excess of iodine in order to ensure the entire removal of acetone. The following method was found to be convenient and to give good results with methyl alcohol containing 0·2 per cent. of acetone : Twenty-five grams of iodine were dissolved in 1 litre of methyl alcohol and the solution was poured slowly and with constant shaking into 500 c.c. of *N*-sodium hydroxide. It was sometimes found necessary to add in addition as much as 150 c.c. of water to precipitate the iodoform, the variable amount being due doubtless to changes of the laboratory temperature. The solution was kept over-night and filtered. The filtrate was yellow, due probably to resin, as the colour deepened on boiling. Dissolved iodoform was hydrolysed by heating under reflux until the smell was absent, and the mixture then fractionally distilled. The first fractionation yielded 800 c.c. of 97 per cent. and 150 c.c. of 85 per cent. acetone-free alcohol.

Since this work was completed a paper on a similar method of purifying methyl alcohol by means of sodium hypochlorite has been published by R. C. Menzies (T., 1922, **121**, 2787).

Summary.

1. The accuracy of Messinger's method of estimating acetone in methyl alcohol has been investigated and the zero error determined for standard conditions.

2. Sodium hypiodite and methyl alcohol react to form some iodoform and probably other products, the incompleteness of the reaction between them being due to the rapid autoxidation of the former to iodate.

3. A convenient and efficient method has been evolved for removing acetone from methyl alcohol by means of sodium hypiodite.

The authors desire to thank Dr. M. A. Whiteley for her help in connexion with this work.

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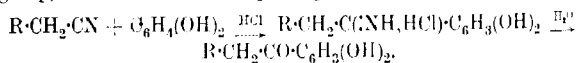
[Received, December 22nd, 1922.]

L.—Di- and Tri-hydroxydeoxybenzoins.

By ERNEST CHAPMAN and HENRY STEPHEN.

HYDROXYDEOXYBENZOINS of the type $C_6H_5 \cdot CH_2 \cdot CO \cdot C_6H_{3-4}(OH)_n$ (where $n = 1, 2$, or 3) had previously been prepared by two general methods: (1) fusing phenylacetic acid with the necessary phenolic compound in the presence of zinc chloride according to Nencki and Sieber's method (*J. pr. Chem.*, 1881, [ii], **23**, 147, 537, 546; 1883, [ii], **25**, 273) of preparing aromatic hydroxy-ketones (Weisl. *Monatsh.*, 1905, **26**, 984; Finzi, *ibid.*, 1905, **26**, 1125; Noelting and Kädler, *Ber.*, 1906, **39**, 2056), or (2) by a modification of Friedel and Crafts' reaction, condensing acid chlorides with phenols, dissolved in nitrobenzene, in the presence of aluminium chloride (Behn, D.R.-P. 95901; Weisl, *loc. cit.*; Finzi, *loc. cit.*).

Substances of this type have now been obtained by applying Hoesch's method (*Ber.*, 1915, **48**, 1122) to the condensation of a cyanide, $R \cdot CH_2 \cdot CN$ (where R is a phenyl or substituted phenyl group) with resorcinol and phloroglucinol:



By this method the following ketones have been prepared :

(I) 2 : 4-Dihydroxydeoxybenzoin (2 : 4-dihydroxyphenyl benzyl ketone), $C_6H_5 \cdot CH_2 \cdot CO \cdot C_6H_3(OH)_2$.

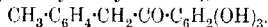
(II) 4'-Chloro-2 : 4-dihydroxydeoxybenzoin (2 : 4-dihydroxy-phenyl-*p*-chlorobenzyl ketone), $C_6H_4Cl \cdot CH_2 \cdot CO \cdot C_6H_3(OH)_2$.

(III) 2 : 4-Dihydroxy-4'-methyldeoxybenzoin (2 : 4-dihydroxy-phenyl *p*-methylbenzyl ketone), $CH_3 \cdot C_6H_4 \cdot CH_2 \cdot CO \cdot C_6H_3(OH)_2$.

(IV) 2 : 4 : 6-Trihydroxydeoxybenzoin (2 : 4 : 6-trihydroxy-phenyl benzyl ketone), $C_6H_3 \cdot CH_2 \cdot CO \cdot C_6H_2(OH)_3$.

(V) 4'-Chloro-2 : 4 : 6-trihydroxydeoxybenzoin (2 : 4 : 6-trihydroxyphenyl *p*-chlorobenzyl ketone), $C_6H_3Cl \cdot CH_2 \cdot CO \cdot C_6H_2(OH)_3$.

(VI) 2 : 4 : 6-Trihydroxy-4'-methyldeoxybenzoin (2 : 4 : 6-trihydroxyphenyl *p*-methylbenzyl ketone),



2 : 4-Dihydroxydeoxybenzoin (the so-called 1-meta-compound), melting at 104° , had been obtained by Finzi (*loc. cit.*), who found it to be identical in all properties except the melting point with the dihydroxydeoxybenzoin (m. p. 115°) obtained by Bülow and Grotowsky (*Ber.*, 1902, **35**, 1527) on heating 7-hydroxy-2-phenyl-4-benzylidene-1 : 4-benzopyranol with a strong aqueous solution of sodium hydroxide. The 2 : 4-dihydroxydeoxybenzoin now prepared agrees in general properties with that obtained by the previous workers and melts at 115° .

The dihydroxydeoxybenzoins were characterised by the preparation of their oximes and diacetyl derivatives, and it was found that such derivatives of 2 : 4-dihydroxydeoxybenzoin differ from the corresponding products obtained by Finzi (*loc. cit.*).

The deoxybenzoins now prepared by Hoesch's method are colourless or very faintly coloured compounds, crystallising from a large volume of hot water in glistening plates. The members of the trihydroxy-series appear to crystallise with one or, in the case of the *p*-methyl compound, one and a half molecules of water. They are readily soluble in most organic solvents except ligroin and petroleum. They are almost insoluble in cold water, but dissolve readily in concentrated sulphuric acid. They are soluble in dilute sodium hydroxide solution, the dihydroxydeoxybenzoins giving colourless solutions and the trihydroxy-compounds yellow solutions. They reduce Fehling's solution on boiling, probably forming the corresponding benzils (compare Finzi, *loc. cit.*, p. 1129). Their alcoholic solutions give deep reddish-brown colorations with a drop of ferric chloride solution, and their solutions in alcohol or ether give a bright red coloration with sodium hypochlorite solution. The oximes give an almost black coloration with ferric chloride,

and with sodium hypochlorite distinctive purple colours. The diacetyl derivatives produce no coloration with ferric chloride and a golden-yellow colour with sodium hypochlorite on long standing.

EXPERIMENTAL.

2 : 4-Dihydroxydeoxybenzoin (I).—Ten grams of resorcinol (1 mol.) and 10 grams of dry, freshly-distilled phenylacetonitrile were dissolved in 60 c.c. of dry ether, 4 grams of powdered zinc chloride added, and the solution treated with a moderately rapid stream of dry hydrogen chloride for two hours under reflux. The closed vessel was left over-night and a few crystals, probably of 2 : 4-dihydroxyphenyl benzyl ketimine hydrochloride, had then separated from the lower, syrupy layer. The mixture was treated with 80 c.c. of 5*N*-hydrochloric acid and extracted with ether to remove any unchanged substances. The aqueous solution was heated on the steam-bath for a short time and a brown oil separated. The aqueous layer was removed when cold and the brown layer again boiled with water. On cooling, glistening plates were deposited and the oil became solid. The dihydroxydeoxybenzoin was filtered off and recrystallised from dilute alcohol or a large quantity of boiling water, the latter proving to be the better solvent for removing impurities.

The reaction was also carried out in a slightly different manner by pouring off the ethereal layer from the mixture after remaining over-night and boiling the semi-solid oily layer directly with water, without using hydrochloric acid.

2 : 4-Dihydroxydeoxybenzoin crystallises from water as colourless, glassy elongated plates, m. p. 115° (Found : C = 73.8; H = 5.30. Calc., C = 73.7; H = 5.30 per cent.).

The *oxime* was prepared by dissolving 3 grams of 2 : 4-dihydroxydeoxybenzoin in 50 c.c. of absolute alcohol and adding a solution of 0.9 gram of hydroxylamine hydrochloride and 1.8 grams of sodium acetate in the smallest possible amount of water. The mixture was heated on the steam-bath for several hours under reflux, the alcohol was removed by evaporation, and the crystalline residue was washed with water and dissolved in warm alcohol. The *oxime*, precipitated on addition of water to this solution, was recrystallised from dilute alcohol as pale brown, hexagonal crystals melting at about 230° with decomposition (Found : C = 68.8; H = 5.55; N = 5.84. Calc., C = 69.1; H = 5.39; N = 5.76 per cent.).

A second crop of crystals was obtained by concentrating the mother-liquor, and these softened at 110° , but did not melt until 210° , recalling Finzi's so-called *oxime*. Microscopic examination

of this product showed it to be a mixture of crystals of the oxime and the unchanged deoxybenzoin, and these were partly separated by fractional crystallisation.

Finzi describes the oxime as fine, yellow needles showing no sharp melting point, but sintering at 110° and partly melting at 170° . It seems probable, therefore, that his product contained unchanged dihydroxydeoxybenzoin (m. p. 115°), which would account for the sintering at 110° .

The *diacetyl* derivative was prepared by boiling 3 grams of 2 : 4-dihydroxydeoxybenzoin with excess of acetic anhydride for four hours and then heating the solution on the steam-bath with the addition of small quantities of methyl alcohol to remove unchanged acetic anhydride. After evaporating the greater part of the solution and cooling, white crystals were deposited. These were recrystallised from hot alcohol, and about 2.5 grams of the compound obtained as colourless, rhombic prisms, m. p. 136° [Found : $\text{CH}_3\cdot\text{CO} = 27.65$, 27.55 . $\text{C}_{14}\text{H}_{10}\text{O}_3(\text{CO}\cdot\text{CH}_3)_2$ requires $\text{CH}_3\cdot\text{CO} = 27.56$ per cent.].

It is insoluble in cold aqueous sodium hydroxide and its alcoholic solution gives no coloration with ferric chloride solution. Finzi, however, by treating the dihydroxydeoxybenzoin with acetyl chloride in pyridine solution, obtained a substance crystallising in white needles, m. p. 107° , which he stated was the diacetyl derivative. From his analysis of the substance, the percentages of carbon, hydrogen, and acetyl are those required for the formula $\text{C}_{18}\text{H}_{16}\text{O}_7$, and do not agree with the formula $\text{C}_{14}\text{H}_{10}\text{O}_3(\text{CO}\cdot\text{CH}_3)_2$. A repetition of Finzi's experiment gave a very small quantity of white needles, m. p. 107° , which were more soluble in alcohol than the diacetyl derivative melting at 136° and also slightly soluble in alkalis [Found : $\text{CH}_3\cdot\text{CO} = 17.1$. $\text{C}_{14}\text{H}_{11}\text{O}_3(\text{CO}\cdot\text{CH}_3)$ requires $\text{CH}_3\cdot\text{CO} = 15.9$ per cent.]. An alcoholic solution of the substance gave a reddish-violet colour with ferric chloride solution. Finzi's product was probably the monoacetyl derivative.

4'-Chloro-2 : 4-dihydroxydeoxybenzoin (II).—*p*-Chlorophenylacetonitrile was prepared by Walther and Hirschberg's method (*J. pr. Chem.*, 1903, [ii], 67, 377).

A solution of 11 grams (1 mol.) of resorcinol and 15 grams (1 mol.) of *p*-chlorophenylacetonitrile in dry ether (60 c.c.), to which 4 grams of powdered zinc chloride had been added, was treated for about five hours with a stream of dry hydrogen chloride. After remaining over-night, the mixture was treated with 100 c.c. of 5*N*-hydrochloric acid and extracted with ether, and the aqueous layer warmed to remove dissolved ether. On cooling, the ketimine hydrochloride separated as a solid mass, which was filtered, washed with a little ether,

hydrolysed by boiling with water, and gave pale brown crystal of 4'-chloro-2:4-dihydroxydeoxybenzoin, m. p. 153—154° (Found: Cl = 13.0.* $C_{14}H_{11}O_3Cl$ requires Cl = 13.5 per cent.).

Its *oxime*, prepared by means of hydroxylamine hydrochloride and sodium acetate, crystallises from dilute alcohol as fine, white, prismatic needles, m. p. 235—236° with decomposition (Found: Cl = 12.75; N = 5.13. $C_{14}H_{12}O_3NCl$ requires Cl = 12.77; N = 5.05 per cent.).

The *diacetyl* compound was obtained by treating 4'-chloro-2:4-dihydroxydeoxybenzoin with acetic anhydride in the manner already described. It was crystallised from alcohol as white, rhombic prisms, m. p. 145° (Found: Cl = 10.0; $CH_3CO = 25.1$, 25.0. $C_{18}H_{15}O_5Cl$ requires Cl = 10.2; $CH_3CO = 24.8$ per cent.).

2:4-Dihydroxy-4'-methyldeoxybenzoin (III).—*p*-Methylbenzyl chloride was prepared from toluene, formaldehyde, and hydrogen chloride by Stephen, Short, and Gladding's method (T., 1920, 417, 522), and was converted into the corresponding cyanide by treatment with sodium cyanide in methyl alcoholic solution.

Eleven grams (1 mol.) of resorcinol and 13 grams (1 mol.) of *p*-tolylacetonitrile were dissolved in dry ether, 4 grams of powdered zinc chloride added, and a stream of dry hydrogen chloride passed in for several hours. The mixture was hydrolysed as already described, but the crude product could not be crystallised from hot water. It was therefore dissolved in a mixture of ether and benzene and the solution dried. On evaporating the ether, the deoxybenzoin separated from the benzene, on cooling, in reddish-brown crystals. Crystallised from dilute alcohol or a large volume of boiling water, it forms colourless, glistening needles, m. p. 114° (Found: C = 74.7, 74.4; H = 5.74, 5.88. $C_{15}H_{14}O_3$ requires C = 74.4; H = 5.82 per cent.).

Its *oxime*, prepared in the usual way, crystallised from dilute alcohol in white, prismatic needles, m. p. 218° with decomposition (Found: C = 69.9; H = 5.92; N = 4.89, 4.92. $C_{15}H_{15}O_3N$ requires C = 70.0; H = 5.88; N = 5.45 per cent.).

The *diacetyl* compound was obtained by treating the deoxybenzoin with acetic anhydride. It crystallises from alcohol as colourless, rhombic prisms, m. p. 112—113° (Found: $CH_3CO = 26.5$. $C_{19}H_{18}O_5$ requires $CH_3CO = 26.4$ per cent.).

2:4:6-Trihydroxydeoxybenzoin (IV).—A solution of 6.3 grams (1 mol.) of anhydrous phloroglucinol and 5.8 grams (1 mol.) of phenylacetonitrile in 50 c.c. of dry ether, to which 3 grams of powdered zinc chloride had been added, was treated for several

* Robertson's (T., 1915, 107, 902) method was used throughout for chlorine estimations.

hours with a stream of dry hydrogen chloride. After standing over-night, the mixture was warmed on the steam-bath, causing complete separation into two layers and evolution of hydrogen chloride. The ethereal layer was removed and the viscous residue hydrolysed by boiling with water for an hour. The crude product, which separated on cooling, was crystallised from a large volume of boiling water, giving colourless, elongated prisms containing one molecule of water of crystallisation which is lost on heating the crystals at 90° . The anhydrous compound melts at 162° (Found: loss at $90-100^{\circ} = 6.97, 6.80$. $C_{14}H_{12}O_4 \cdot H_2O$ requires $H_2O = 6.94$ per cent. Found: in anhydrous compound, $C = 68.76$; $H = 5.00$. $C_{14}H_{12}O_4$ requires $C = 68.84$; $H = 4.95$ per cent.).

4'-Chloro-2:4:6-trihydroxydeoxybenzoin (V).—A solution of 11 grams (1 mol.) of *p*-chlorophenylacetonitrile and 9.2 grams (1 mol.) of anhydrous phloroglucinol in 70 c.c. of dry ether, after the addition of 4 grams of powdered zinc chloride, was treated with a stream of dry hydrogen chloride for four hours, and the mixture hydrolysed with water as already described. The deoxybenzoin was crystallised from boiling water in colourless needles containing one molecule of water of crystallisation. The anhydrous substance melts at $221-222^{\circ}$ (Found: $H_2O = 6.01, 6.11$. $C_{14}H_{11}O_4Cl \cdot H_2O$ requires $H_2O = 6.10$ per cent. Found in anhydrous compound, $Cl = 12.3, 12.6$. $C_{14}H_{11}O_4Cl$ requires $Cl = 12.7$ per cent.).

2:4:6-Trihydroxy-4'-methyldeoxybenzoin (VI).—A solution of 12.6 grams of anhydrous phloroglucinol and 13.1 grams of *p*-tolylacetonitrile in dry ether, treated by the method already described, yielded the deoxybenzoin, which was recrystallised from hot water in slightly pink, transparent plates containing one and a half molecules of water of crystallisation. The anhydrous substance melts at $205-206^{\circ}$ (Found: $H_2O = 9.70, 9.69$. $C_{15}H_{14}O_4 \cdot 1\frac{1}{2}H_2O$ requires $H_2O = 9.48$ per cent. Found: in anhydrous compound, $C = 69.7$; $H = 5.48$. $C_{15}H_{14}O_4$ requires $C = 69.8$; $H = 5.47$ per cent.).

In conclusion, one of us (E. C.) desires to thank the Advisory Council of the Department of Scientific and Industrial Research for a grant which has enabled him to participate in this work.

THE CHEMICAL DEPT.,

THE UNIVERSITY, MANCHESTER.

[Received, December 6th, 1922.]

hours with a stream of dry hydrogen chloride. After standing over-night, the mixture was warmed on the steam-bath, causing complete separation into two layers and evolution of hydrogen chloride. The ethereal layer was removed and the viscous residue hydrolysed by boiling with water for an hour. The crude product, which separated on cooling, was crystallised from a large volume of boiling water, giving colourless, elongated prisms containing one molecule of water of crystallisation which is lost on heating the crystals at 90° . The anhydrous compound melts at 162° (Found: loss at $90-100^{\circ} = 6.97$, 6.80 . $C_{14}H_{12}O_4 \cdot H_2O$ requires $H_2O = 6.94$ per cent. Found: in anhydrous compound, $C = 68.76$; $H = 5.00$. $C_{14}H_{12}O_4$ requires $C = 68.84$; $H = 4.95$ per cent.).

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THE CHEMICAL DEPARTMENT,

THE UNIVERSITY, MANCHESTER.

[Received, December 6th, 1922.]

LI.—*Determination of the Isoelectric Point of Gelatin.
A Criticism of Patten and Kellems's Method.*

By THOMAS SLATER PRICE.

IN the course of measurements of the hydron concentration of various gelatin solutions, Patten and Kellems (*J. Biol. Chem.*, 1920, 42, 363) used a method for plotting their results which has apparently led them to the conclusion that different gelatins have different isoelectric points which can be determined directly by electrometric titration. Their method of experiment was as follows: Solutions were made up containing 0.5 per cent. of gelatin and different concentrations of hydrochloric acid (or sodium hydroxide), and their hydron concentrations measured electrometrically in each case. The results obtained for two different gelatins are given in the following table, the figures for the p_H in ordinary type referring to an ashless gelatin, whilst those in italics refer to a commercial gelatin.

Normality with respect to HCl.	p_H .		Normality with respect to NaOH.	p_H .	
10^{-1}	0.77	0.96	0.0	4.81	5.6
10^{-2}	1.96	2.12	10^{-6}	4.89	5.54
10^{-3}	3.89	4.49	10^{-5}	5.00	5.65
10^{-4}	4.69	5.4	10^{-4}	5.06	5.69
10^{-5}	4.74	5.6	10^{-3}	6.49	8.78
10^{-6}	4.83	5.6	10^{-2}	11.33	11.57

Patten and Kellems then use the following method to plot their results. The p_H 's of the various solutions are taken as ordinates and the normalities of the total system with respect to acid (or alkali) as abscissæ. To avoid excessive use of ciphers the negative exponent of the normality is used; thus, where the normality is 1×10^{-6} , the figure 6 is used as the abscissa. The curves thus obtained are shown in the figure.

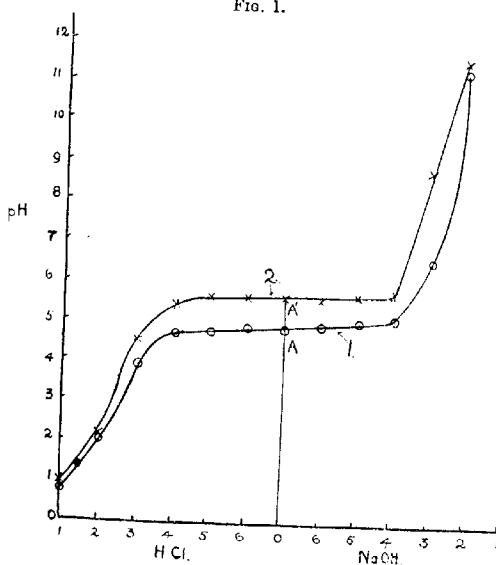
Patten and Kellems then state: "It will be observed that the isoelectric point of ash-free gelatin, Curve 1, lies at $p_H = 4.8$, corresponding with a hydron concentration of 1.59×10^{-5} , and that the isoelectric point of commercial gelatin, Curve 2, lies further toward the alkaline region and comes at $p_H = 5.64$ (hydron concentration, 2.28×10^{-6})."^{*} This statement that the horizontal portions of the curves indicate different isoelectric points is apparently made simply because those parts are horizontal. Consideration of the curves will show, however, that the method of plotting cannot give anything else but an approximately straight-

^{*} Patten and Kellems's paper gives 2.28×10^{-5} , which is a misprint for 2.28×10^{-6} .

line central portion, since the abscissæ, as well as the ordinates, are plotted on a logarithmic scale. There is a very good reason for plotting the ordinates (p_H 's) on a logarithmic scale, since the electrometric method of determining hydrion concentrations gives a direct measurement of their logarithmic concentration, but no such reason can be adduced for similarly plotting the normalities of the total system.

That the results obtained are purely fictitious, as far as the determination of the isoelectric point is concerned, can be shown

FIG. 1.



reference to the figure, as follows. The ashless gelatin, to which either acid nor alkali has been added, has p_H 4.81 (point A). Similarly the commercial gelatin has p_H 5.6 (point A'). Addition of 10^{-6} acid or alkali will give points to the left or right of A and A' of practically the same p_H , since the amount of acid or alkali added is so very small. Similarly for 10^{-5} acid or alkali, and so on, the effect of the addition of acid or alkali on the p_H only beginning to show when their concentrations are about 10^{-3} N. A straight-line central portion of the curve is thus obtained,* the position of which

* If the results are plotted using a normality instead of a log-normality scale as abscissæ, it will be seen that the straight-line portion of the curve compresses to what is practically a point of inflexion.

has really nothing to do with the isoelectric condition of gelatin, but is really fixed by the p_H of the gelatin started with and to which neither acid nor alkali has been added. The mistake made by Patten and Kellems is in taking the points A and A' as both corresponding with 0 on the abscissæ. In the case of the commercial gelatin it is impossible to say what was the normality with respect to hydrochloric acid or sodium hydroxide, owing to the unknown alkalinity of the gelatin taken. As a matter of fact, they show later in their paper that the commercial gelatin was really alkaline. What, in reality, their method does, is to show that it requires more acid to give a definite p_H to the commercial than to the ashless gelatin, a result which is obvious in view of the alkali content of the former gelatin.

That one is bound to obtain results similar to those of Patten and Kellems has been shown by Mr. S. O. Rawling in some (unpublished) experiments he has carried out. A 2 per cent. solution of ash-free gelatin was first titrated with hydrochloric acid, the p_H of the system being measured after each addition of acid. A solution of the same concentration of gelatin, to which a small amount of sodium hydroxide had been added, was similarly titrated. The curves obtained were similar to those of Patten and Kellems when plotted according to their method.

Sheppard, Sweet, and Benedict (*J. Amer. Chem. Soc.*, 1922, 44, 1857) have made use of the same method to determine the isoelectric point of ash-free gelatins to which various small amounts of alum had been added. They find that the so-called isoelectric point occurs at decreasing values of the p_H as the concentration of the alum increases. From what has been said above this result is to be expected, since owing to the hydrolysis of the alum the solutions are acid.

The author has been in correspondence with Dr. Sheppard, who expresses his agreement with the considerations put forward above.

THE BRITISH PHOTOGRAPHIC RESEARCH ASSOCIATION LABORATORIES.

[Received, January 5th, 1923.]

LII.—*The Propagation of Flame in Complex Gaseous Mixtures. Part V. The Interpretation of the Law of Speeds.*

By WILLIAM PAYMAN.

THE addition of the incombustible gas nitrogen to the mixture of methane and oxygen of the composition $\text{CH}_4 + 2\text{O}_2$ results in a reduction of the speed of uniform movement of flame in the mixture.

Both methane and oxygen behave similarly to nitrogen in that they also reduce the speed of uniform movement of flame when added to this mixture (T., 1920, 117, 56).

The speed of the uniform movement of flame, under standard experimental conditions, in a mixture of any given inflammable gas with air or oxygen depends on the rate of reaction in that mixture, and is mainly determined, therefore, by the temperature of the burning gases (*loc. cit.*, p. 49). It follows that with a given mixture (such, for example, as $\text{CH}_4 + 2\text{O}_2$) the greater the cooling effect of a gas added to the mixture the greater will be its retarding effect on the speed of the flame. Thus, methane, having the highest specific heat of the gases methane, oxygen, and nitrogen, is found to have the most marked retarding effect of the three.

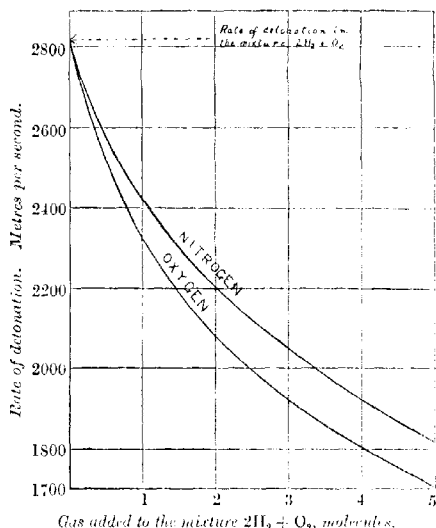
If the retarding action of an added gas were dependent solely on its cooling effect, that is to say, on its specific heat, a simple explanation could be offered for the Law of Speeds (T., 1922, 121, 364). A mixture with a given speed of flame may be obtained by adding a certain volume of methane to the mixture $\text{CH}_4 + 2\text{O}_2$. A different mixture having the same speed of flame may be obtained by adding a different volume of nitrogen to the same unit volume of $\text{CH}_4 + 2\text{O}_2$. These different volumes of methane and of nitrogen would, perforce, have the same heat capacity if this supposition were correct; that is to say, they would require the same amount of heat to raise them to the temperature of the burning gases. A complication is, however, introduced by the effect of mass-action. The probable magnitude of this effect will be considered later; in the meantime, it will simplify discussion to neglect it.

Since these two volumes, the one of methane, the other of nitrogen, have the same heat capacity, then a given proportion of the one could be replaced by the same proportion of the other without altering the total heat capacity of either, or altering the retarding effect of either on the speed of flame.

This is in effect what is done when two gas mixtures having the same speed of flame are mixed together. A simple example will help to make this clear. Imagine two mixtures with the same speed of flame produced by diluting the basic mixture $\text{CH}_4 + 2\text{O}_2$ with either methane or nitrogen, the composition of the one being $\text{CH}_4 + 2\text{O}_2 + x\text{CH}_4$, and that of the other being $\text{CH}_4 + 2\text{O}_2 + y\text{N}_2$. It follows that $x\text{CH}_4$ and $y\text{N}_2$ will have the same heat capacity. Now, if half the diluting gas in the first mixture is replaced by half the diluting gas in the second mixture, the resulting mixture will have the composition $\text{CH}_4 + 2\text{O}_2 + \frac{x}{2}\text{CH}_4 + \frac{y}{2}\text{N}_2$. The quantity of diluting gas is now $\frac{y}{2}\text{CH}_4 + \frac{y}{2}\text{N}_2$; this will have the same heat

capacity as either $x\text{CH}_4$ or $y\text{N}_2$, and the new mixture will therefore have the same speed of flame as the original mixture. Exactly the same mixture would be obtained by mixing together equal volumes of the original mixtures, giving a mixture of the composition $\text{CH}_4 + 2\text{O}_2 + x\text{CH}_4 + \text{CH}_4 + 2\text{O}_2 + y\text{N}_2$, or 2 volumes of $\text{CH}_4 + 2\text{O}_2 + \frac{x}{2}\text{CH}_4 + \frac{y}{2}\text{N}_2$.* From the law of speeds it is known that this mixture will have the same speed of flame as either of the two original mixtures.

FIG. 1.



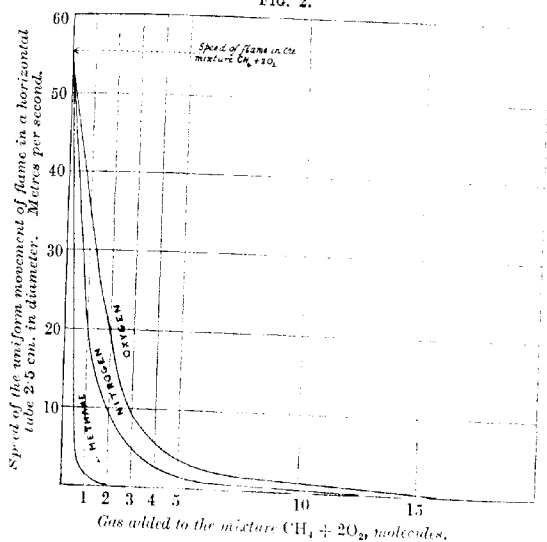
It will be seen that the law of speeds can be explained on the assumption that any addition of incombustible gas, inflammable gas, or oxygen to a mixture of inflammable gas and oxygen in combining proportions has a retarding effect on the speed of the uniform movement of flame proportional to its specific heat.

* It has been emphasised in earlier papers that the law of speeds can only be applied to similar mixtures, containing excess of oxygen or containing excess of inflammable gas. The reason for this will now be apparent, for the mixing together of two unlike mixtures corresponding with, say, $\text{CH}_4 + 2\text{O}_2 + x\text{CH}_4$ and $\text{CH}_4 + 2\text{O}_2 + y\text{O}_2$ will result in alteration of the quantity of the basic mixture, $\text{CH}_4 + 2\text{O}_2$, present. Some of the added methane of the first mixture would combine with some of the added oxygen of the second, and would no longer act as diluting gas, so that the speed of flame would be increased.

This explanation of a law which was first enunciated as a purely empirical relationship, observed between the speeds of the uniform movement of flame in complex gas mixtures, has proved useful in many ways. One of these is the prediction of the application of the law of speeds to other modes of propagation of flame within certain limits.

The diluting or retarding effect of added gas, both combustible and incombustible, to a given gas mixture has its counterpart in the propagation of the explosion-wave. Dixon has shown (*Phil.*

FIG. 2.



Trans., 1893, 184, 97) that the addition of either oxygen or nitrogen to electrolytic gas, $2\text{H}_2 + \text{O}_2$, reduces the rate of detonation in the resulting mixture.* This is shown in Fig. 1, which is reproduced from Dixon's paper (*loc. cit.*, p. 188), and should be compared with Fig. 2, which shows the effect of the addition of methane, oxygen, and nitrogen, to the mixture $\text{CH}_4 + 2\text{O}_2$, on the speed of the uniform movement of flame.

The diluting or retarding effect of the addition of oxygen and

* The explosion wave differs from the uniform movement in that with the former the addition of hydrogen to the mixture $2\text{H}_2 + \text{O}_2$, and of methane to the mixture $\text{CH}_4 + 2\text{O}_2$, increases the rate of detonation, whereas the speed of the uniform movement is decreased in both mixtures.

nitrogen on the rate of detonation of electrolytic gas has been shown by Dixon to be proportional to the respective densities of the gases. Densities are additive properties just as are specific heats; for weights are additive just as are heat capacities. Hence it follows that the law of speeds should hold for the detonation-wave in mixtures of hydrogen, oxygen, and nitrogen in which the oxygen is present in sufficient quantity to burn the hydrogen completely.

In order to test the truth of this conclusion, Professor Dixon kindly allowed a series of experiments to be carried out in his laboratory with a number of mixtures of hydrogen, oxygen, and nitrogen of different compositions, using the original apparatus in which his experiments were carried out. These experiments, which are described in another communication, have shown that the law of speeds holds exactly for the rate of detonation in these mixtures. The fact must be emphasised that the law of speeds applies to these mixtures for a similar, but not the same, reason for which it applies to the uniform movement of flame.

This reason for the application of the law of speeds to the uniform movement of flame also serves to explain certain peculiarities observed in the results of the early experiments that were made to test the truth of the law. It was found that the law did not hold exactly with all gaseous mixtures. Appreciable differences, small, but beyond the limits of possible experimental error, were found between the observed and calculated values for the speeds of flame in complex gas mixtures. There was evidently some other factor which either prevents or assists to a slight extent the retarding effect of the added gas or gases.

We have assumed in the reasoning outlined above that the rate of reaction is dependent entirely on the temperature of the reacting gases, and that in mixtures of one particular gas and air or oxygen the mixture with the highest temperature will also have the highest speed of flame. The rate of reaction, however, will also depend on the concentrations of the reacting gases. It has been shown (T., 1920, 117, 49) that, for a given combustible gas, the mixture with the highest calorific effect is not necessarily the mixture with the maximum speed of flame, which is sometimes obtained in a mixture of different composition. The difference in composition between these mixtures has been termed the "displacement" of the maximum-speed mixture. The nature of the displacements observed confirms the supposition that they are due to the effect of mass action. In the same way it would appear that the small differences between observed and calculated values for the speeds of flame are also due to the effect of mass action.

Reference to Fig. 2 will show that the retarding effect of oxygen on the speed of the uniform movement of flame in the mixture $\text{CH}_4 + 2\text{O}_2$ is rather less than that of nitrogen, although the specific heats of nitrogen and oxygen are approximately the same. The reason for this was suggested in Part IV of this series of papers (*loc. cit.*, p. 56). Since the rate of reaction depends not only on the temperature, but also on the concentrations of the reacting gases, the fact that the oxygen can take part in the reaction will cause its retarding effect to be less than that of another gas of the same specific heat which cannot take place in the reaction; because, although the temperature effect may be the same, the mass-action factor is greater when the diluting gas is reactive, and therefore the rate of reaction in this mixture would be greater. If we consider the two mixtures with the same calorific effect, (1) $\text{CH}_4 + 2\text{O}_2 + x\text{O}_2$, and (2) $\text{CH}_4 + 2\text{O}_2 + y\text{N}_2$, the speed of flame in these two mixtures would be the same if it depended solely on the temperature. If the specific heats of oxygen and nitrogen are assumed to be the same exactly, $x = y$. The mass-action factor is given by the expression $C_{\text{CH}_4} \times C_{\text{O}_2}^2$. If unit quantity of methane* is taken in both mixtures,

$$C_{\text{CH}_4} \times C_{\text{O}_2}^2 = \frac{1}{3+x} \cdot \frac{(2+x)^2}{(3+x)^2} \quad \dots \quad (1)$$

and

$$C_{\text{CH}_4} \times C_{\text{O}_2}^2 = \frac{1}{3+y} \cdot \frac{2^2}{(3+y)^2} \quad \dots \quad (2)$$

Since $x = y$, (1) is always greater than (2), and therefore the rate of reaction is always greater in mixture (1) than in mixture (2), even although the calorific effect of the two mixtures is the same.

Let us now consider what effect the coming into play of mass action will have on the application of the law of speeds in mixtures of two inflammable gases with air or oxygen. It will simplify explanation if a particular example be chosen. The upper limit of methane in air in a horizontal tube, 2.5 cm. in diameter, was found to be 13.3 per cent. The upper-limit mixture of hydrogen in air under similar conditions was found to contain 71.4 per cent. of hydrogen. If from these values the limit for the mixture $\text{CH}_4 + \text{H}_2$ is calculated by means of the law of speeds, the value

* The mass-action factor gives a relative measure of the number of fruitful collisions taking place between inflammable gas and oxygen in unit time. Taking unit quantity of inflammable gas affords a measure of the chances of each molecule of the inflammable gas entering into chemical combination with oxygen in that period.

obtained is 22.4 per cent. The composition of the three limit mixtures is as follows :

	1.	2.	3.
Hydrogen	71.4	—	11.2
Methane	—	13.3	11.2
Oxygen	6.5	18.2	16.3
Nitrogen	22.1	68.5	61.3

The value for the mass-action factor is given by the expression $C_{H_2}^2 \times C_{O_2}$ for the reaction $2H_2 + O_2$, and $C_{CH_4} \times C_{O_2}$ for the reaction $CH_4 + 2O_2$. For unit volumes of methane and hydrogen the factor in each of the three mixtures becomes :

For hydrogen

$$(71.4 \times 71.4 \times 6.5)/71.4 = 464 \quad \text{in (1)}$$

$$\text{and } (11.2 \times 11.2 \times 16.3)/11.2 = 182 \quad \text{in (3)}$$

And for methane

$$(13.3 \times 18.2 \times 18.2)/13.3 = 331 \quad \text{in (2)}$$

$$\text{and } (11.2 \times 16.3 \times 16.3)/16.3 = 265 \quad \text{in (3)}$$

That is to say, the factor for each gas is less in the calculated complex mixture than in each of the simple mixtures.* The speed-law calculation is made, however, on the assumption that the rate of reaction in all three mixtures is the same, since their calorific effects are the same. But the rate of both reactions will be less in the complex mixture, on account of the effect of mass action; instead of this mixture being a limit mixture (that is to say, a mixture just able to support combustion), the result will be that it will not be able to do so, and the mixture must have more air added to it before the rate of reaction becomes sufficiently great, owing mainly to increased temperature, for it to allow of complete and independent propagation of flame. The value found experimentally for the limit in this mixture was 20.8 per cent.

Similarly, if two mixtures having the same speed of flame are mixed together, the resulting mixture will have a slightly lower speed, since the rates of the reactions in this complex mixture will be less than in the respective simple mixtures.

In this illustration limit mixtures have been utilised to simplify the wording. Any mixture of two (similar) mixtures having the same speed of flame could have been chosen; for example, the two mixtures of methane in air and hydrogen in air that have a speed of flame of 50 cm. per second. The law of speeds applies to limit mixtures because the speed of flame in limit mixtures of most

* In other words, the number of fruitful collisions of methane with oxygen and of hydrogen with oxygen in unit time will be less in the complex mixture than in the respective simple mixtures.

inflammable gases in air, taken singly, is approximately the same; when some other speed is chosen, other than the speed at the limits, the same result is obtained.

For case of reference, it is convenient to make use of special mixtures such as "maximum-speed mixtures," "mixtures for complete combustion," or "limit mixtures." Similar calculations with these mixtures indicate that the speed of the uniform movement of flame actually obtained in most of the complex gaseous mixtures which have been examined should be less than that calculated from the law of speeds.

The observed and calculated speeds of flame in maximum-speed mixtures and mixtures for complete combustion are given in Tables I and II, and the differences observed are in agreement with the theory that has been outlined, that is, the actual speeds of flame are less than those calculated.

TABLE I.
Maximum-speed Mixtures.

Mixture.	Maximum speed of uniform movement of flame.		
	Calc.	Found.	Diff.
$3C_2H_{12} + 2H_2$	100	89.5	- 10.5
$CH_4 + C_2H_{12}$	78.5	78.3	- 0.2
$CH_4 + H_2$	150	135	- 15
$3CH_4 + H_2$	99	85	- 14
Coal gas	164	154	- 10
Producer gas	85	72	- 13

TABLE II.
Mixtures for Complete Combustion.

Mixture.	Speed of uniform movement of flame.		
	Calc.	Found.	Diff.
$H_2 + 3CH_4$	95	85	- 10
$H_2 + CH_4$	149	135	- 14
$3H_2 + CH_4$	246	240	- 6

Any factor which reduces the speed of flame in a limit mixture will render that mixture incapable of self-propagation of flame. Hence we would expect that the upper limit of inflammability of a complex mixture would always be less than the value calculated. An actual comparison is given in Table III.

TABLE III.
Upper-limit Mixtures.

Mixture.	Upper limit.		
	Calc.	Found.	Diff.
$3C_2H_{12} + 2H_2$	8.6	8.6	0.0
$CH_4 + C_2H_{12}$	7.7	7.7	0.0
$CH_4 + H_2$	22.4	20.8	- 1.6
$3CH_4 + H_2$	16.7	15.5	- 1.2
Coal gas	26.4	24.3	- 2.1

q* 2

It would be expected that the mass-action effect would become less important when the percentage of oxygen is greatly in excess of that required to burn the inflammable gas completely. Calculation supports this view; thus, in the lower-limit mixture of $\text{CH}_4 + \text{H}_2$ the mass-action factor for unit volume of methane is slightly higher than in the lower-limit mixture of methane alone, and the factor for hydrogen is reduced, but to a much less extent than was seen to obtain with the upper-limit mixtures. Examination of the curves given in earlier papers will show that the agreement between observed and calculated values is quite close when the oxygen is in excess, and the law of speeds has been shown to apply very accurately to lower-limit mixtures.

The law of speeds as applied to the uniform movement during the propagation of flame can therefore be explained on the assumption that the variations in the speed of flame as determined under standard conditions with mixtures of different compositions depends on the rate of reaction between the inflammable gases and oxygen in the flame front. The law of speeds would hold exactly if this rate of reaction was dependent solely on the temperature, so that excess of either inflammable gas, oxygen, or of incombustible gas could be regarded as behaving simply as diluting gas, lowering the reaction temperature, but taking no part in the reaction. The fact that the rate of reaction must also depend on the concentrations of the reacting gases results in small divergences from the law when the oxygen is in deficit. The correction necessary to allow for this cannot be correctly estimated, but the general effect of this factor is to make the speeds of the uniform movement of flame in complex mixtures rather slower than the speeds calculated from the law of speeds.

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[Received, December 21st, 1922.]

LIII.—*The Rate of Detonation in Complex Gaseous Mixtures.*

By WILLIAM PAYMAN and NOEL STANLEY WALLS.

In the preceding paper it was suggested that the law of speeds should apply to the rate of detonation in mixed gases containing sufficient oxygen for the complete combustion of the inflammable gases. The necessity for this limitation will be apparent if we compare the effects of change of composition of a mixture of one inflammable gas with air or oxygen on the speed of propagation of flame during

"detonation" and during the initial, slow, "uniform movement" of flame.

With both phases of propagation there are limits beyond which that mode of propagation cannot be set up. The "limits of inflammability" of an inflammable gas in air or in oxygen can be determined, for any given set of conditions, with great accuracy, but the limits of detonation can only be estimated roughly, since they depend apparently on the mode of ignition, and in mixtures near the limit of detonation there is no positive means of determining whether the flame is propagated by detonation or not (or partly by detonation and partly by other means), since the flame may attain an extremely rapid speed of propagation without detonation being set up.

Interesting and important deductions from the law of speeds are (1) that the addition of any inflammable gas to the lower-limit mixture of the same or any other inflammable gas in air or oxygen will result in an increase in the speed of the uniform movement of flame in the mixture; (2) that addition of inflammable gas to the maximum-speed mixture of any inflammable gas in air or oxygen will result in a reduction of the speed; and (3) that addition of inflammable gas to the upper-limit mixture of any inflammable gas will result in the mixture being rendered incapable of self-propagation of flame.

Herein, so far as the present research is concerned, lies the main distinction between propagation by the uniform movement and by detonation. The addition of inflammable gas to the "lower-limit detonating-mixture" will result in an increase in the rate of detonation in the mixture, but with further increase in the concentration of inflammable gas a point is at last reached when the addition of one inflammable gas may increase the rate whereas the addition of another inflammable gas may reduce it. Thus, the addition of hydrogen to electrolytic gas ($2\text{H}_2 + \text{O}_2$) increases the rate of detonation, whilst addition of carbon monoxide lowers the rate.

There would appear to be no "maximum-rate detonation-mixture" in the same sense as there is a maximum-speed mixture with the uniform movement of flame. Thus, with hydrogen and oxygen the "upper-limit detonating mixture" has a greater rate of detonation than any of the more dilute mixtures. With methane and oxygen the rate of detonation increases with increased percentage of methane until there is 50 per cent. of methane present; with further addition of methane the rate decreases. The rate of detonation in a mixture of methane and oxygen containing 50 per cent. of methane is 2513 metres per second. With 53.3 per cent. of methane, the rate is 2388 metres per second, and with 57.1 per cent.

of methane the detonation-wave is not set up.* It is quite possible that the addition of hydrogen to the "upper-limit detonating mixture" of some other gas might increase the rate of detonation instead of preventing detonation altogether.

It will be evident, then, that any application of the law of speeds to propagation by the explosion-wave will necessarily be limited.

Only that portion of the law of speeds which has been termed the "speed generalisation" will apply to this phase (T., 1919, 115, 1447); that portion dealing with "limit mixtures" and with "maximum-speed mixtures" will not apply. The application of the law of speeds is also limited to mixtures of the same kind, containing excess of oxygen or excess of inflammable gas. With the mixtures used for the present research this restricts us to using only mixtures containing excess of oxygen.

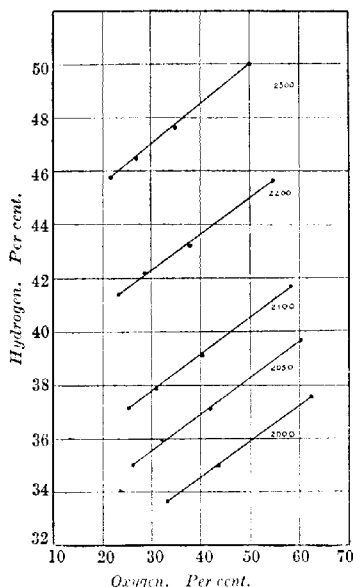
Two series of experiments have been carried out, and the procedure in both was similar to that adopted in the work on the speed of the uniform movement of flame in complex

gaseous mixtures. The first measurements of the rate of detonation

* The maximum and minimum speeds of propagation of flame (1) in the detonation-wave and (2) during the uniform movement of flame in a horizontal tube 2.5 cm. in diameter are given in the following table, which illustrates in an interesting manner the differences to which reference has been made.

	(1)		(2)	
	Detonation-wave.		Uniform movement.	
		Speed of flame.		Speed of flame.
	Methane.	Metres	Methane.	Metres
	Per cent.	per sec.	per cent.	per sec.
Lower-limit mixture	11.1	1678	5.7	0.199
Upper-limit mixture	53.3	2388	59.2	0.189
Maximum-speed mixture	50.0	2508	33.3	55

FIG. 1.



were made with mixtures of hydrogen, oxygen, and nitrogen. As in the determinations of the speed of the uniform movement of flame in mixtures of methane, oxygen, and nitrogen (T., 1920, 117, 52), different "atmospheres" or mixtures of oxygen and nitrogen were first prepared. The rates of detonation were then measured in a number of mixtures of the inflammable gas—hydrogen in this series of experiments—with each of these atmospheres. The method of measurement and the apparatus used were exactly the same as those used by Dixon (*Phil. Trans.*, 1893, 184, 97).

The results are given in Table I. The values obtained were plotted on a speed-percentage graph and by interpolation the compositions of the different mixtures having a given rate of detonation were obtained. It has been shown (T., 1919, 115, 1439) that if the law of speeds holds with mixtures of an inflammable gas, oxygen, and nitrogen, then, if the compositions of different mixtures having a given speed of flame are plotted on a graph whose axes represent the composition of the mixture, all the values (for mixtures of the same kind) will lie on a straight line. Such a graph is shown in Fig. 1, for a number of different rates of detonation, percentages of hydrogen being plotted against percentages of oxygen.

TABLE I.

Rates of Detonation in Mixtures of Hydrogen, Oxygen, and Nitrogen.

Atmosphere 100 per cent. O ₂ .			
Hydrogen. Per cent.	Oxygen. Per cent.	Rate of detonation. Metres per second.	
22.2	77.8	1600	
25.0	75.0	1693	
33.3	66.7	1917	
50.0	50.0	2311	
66.7	33.3	2817	
80.0	20.0	3278	
85.5	14.5	3527	
88.9	11.1	3532	
Atmosphere 66.6 per cent. O ₂ .			
Hydrogen. Per cent.	Oxygen. Per cent.	Nitrogen. Per cent.	Rate of detonation. Metres per second.
25.0	50.0	25.0	1756
33.3	44.4	22.3	1961
50.0	33.3	16.7	2374
66.6	22.2	11.2	2822
75.0	16.7	8.3	3090
80.0	13.3	6.7	3137
Atmosphere 50 per cent. O ₂ .			
Hydrogen. Per cent.	Oxygen. Per cent.	Nitrogen. Per cent.	Rate of detonation. Metres per second.
33.3	33.3	33.3	1990
50.0	25.0	25.0	2388
66.6	16.6	16.6	2767
75.0	12.5	12.5	2846

TABLE I.—(continued).

Atmosphere 40 per cent. O ₂ .			
Hydrogen. Per cent.	Oxygen. Per cent.	Nitrogen. Per cent.	Rate of detonation. Metres per second.
33.3	26.6	40.1	2016
50.0	20.0	30.0	2383
66.6	13.3	20.1	2655
71.4	11.4	17.2	2675

The dots represent values interpolated from the experimental results in the manner already described. The diagram shows clearly that the law of speeds holds for the rates of detonation in mixtures of hydrogen, oxygen, and nitrogen when the oxygen is present in sufficient quantity to burn the hydrogen completely to steam.

TABLE II.

Rates of Detonation in Mixtures of Methane, Hydrogen, and Oxygen.

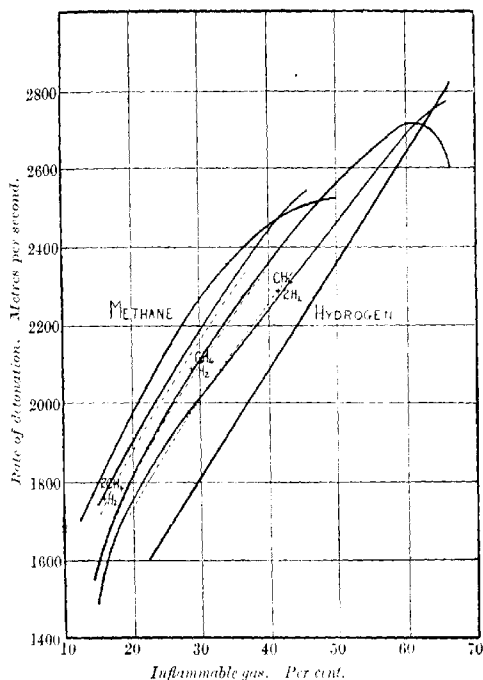
Methane.		2CH ₄ + H ₂ .	
Methane. Per cent.	Rate of detonation. Metres per second.	Inflammable gas. Per cent.	Rate of detonation. Metres per second.
11.1	1678	14.3	1728
20.0	1980	25.0	2050
25.0	2146	40.0	2444
33.3	2337	46.1	2546
40.0	2465	50.0	2605
50.0	2513	54.5	2679
53.3	2388	60.0	2600

CH ₄ + H ₂ .		CH ₄ + 2H ₂ .	
Inflammable gas. Per cent.	Rate of detonation. Metres per second.	Inflammable gas. Per cent.	Rate of detonation. Metres per second.
13.8	1532	14.3	1449
21.0	1875	15.8	1582
44.4	2464	16.7	1666
50.0	2561	20.0	1764
57.1	2697	33.3	2094
66.7	2604	50.0	2474
		54.5	2572
		66.7	2782

Hydrogen.	
Hydrogen. Per cent.	Rate of detonation. Metres per second.
22.2	1600
25.0	1693
33.3	1917
50.0	2311
66.7	2817
80.0	3278
85.5	3527
88.9	3532

The second series of determinations was carried out with mixtures of methane and hydrogen with oxygen. As in the experiments on the speed of the uniform movement of flame, different mixtures of methane and hydrogen were first prepared, and the rates of detonation then measured in a series of mixtures of each methane-hydrogen mixture with oxygen. The results obtained are given in Table II.

FIG. 2.



The rates given are the mean of a series of determinations with each mixture. The accuracy with which a determination could be repeated differed with different mixtures, but the maximum difference observed in any one series with the same mixture was about 30 metres per second, a difference of between 1 and 2 per cent. on the speeds measured.

The results are plotted in Fig. 2. The dotted lines show the values for the intermediate mixtures, calculated by means of the law of

speeds, for mixtures containing excess of oxygen. Good agreement is shown with the mixtures $\text{CH}_4 + \text{H}_2$ and $\text{CH}_4 + 2\text{H}_2$. The calculated values are uniformly low by 20 to 30 metres per second with the mixture $2\text{CH}_4 + \text{H}_2$; that is to say, from 1 to 2 per cent. on the speed measured, but this difference is not greater than the greatest experimental difference in the recorded speeds.

The law of speeds therefore applies, within the limits of experimental error, to the rate of detonation in mixtures of hydrogen, oxygen, and nitrogen, and in mixtures of methane and hydrogen in oxygen in which the oxygen is present in sufficient quantity to burn the inflammable gas completely to steam or to carbon dioxide and steam.

There remains the not unlikely possibility that the law of speeds will apply to other, non-uniform phases in the propagation of flame. This will be examined during the course of other work, carried out with the main intention of investigating other problems of flame propagation and gaseous explosions.

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[Received, December 21st, 1922.]

LIV.—*The Effect of Pressure on the Limits of Inflammability of Mixtures of the Paraffin Hydrocarbons with Air.*

By WILLIAM PAYMAN and RICHARD VERNON WHEELER.

It has been shown by Mason and Wheeler (T., 1918, **113**, 45) that the effect of increased initial pressure, above atmospheric, on the limits of inflammability of hydrogen and of carbon monoxide in air is to narrow the limits on both sides; that is to say, more inflammable gas is necessary to form a lower-limit mixture and more air is necessary to form an upper-limit mixture. This was also found to be so with methane at the lower limit, but the upper limit was extended as the pressure was increased.

It had been anticipated, from the law of mass action, that increase of pressure would extend both limits with all gases. The most probable explanation for the observed narrowing of the limits in most instances would appear to be that suggested by Terres and Plenz (*J. Gasbeleucht.*, 1914, **57**, 990, 1001, 1016, 1025), namely, that loss of heat from a gas at high pressure is due to a greater extent to convection than to conduction, and increases with the pressure. If this explanation is correct, the behaviour of the mixtures of

methane and air under high pressures at the upper limit must be regarded as abnormal, and demands further study.

In the present research the experiments have been continued in order to find out whether mixtures of air with other paraffin hydrocarbons would behave in the same manner as methane-air mixtures. Experiments have also been carried out to test further the suggestion of Terres and Plenz regarding the transference of heat by convection at high pressures. The experimental method was the same as that used by Mason and Wheeler, except that a longer glass tube (40 cm. instead of 18 cm.) of 2 cm. internal diameter was used. The criterion of inflammability was, as before, propagation of flame downwards. The results of the first series of experiments are given in Tables I and II.

TABLE I.
Lower Limits.

Downward propagation of flame.

(a) Ethane.		(b) Propane.	
Pressure. mm.	Limit. Per cent.	Pressure. mm.	Limit. Per cent.
760	3.13	760	2.40
1700	3.13	940	2.36
2150	3.15	2620	2.36
3440	3.19	3400	2.40
4260	3.22	4270	2.44
Ethane 3.24 per cent. : Complete propagation at all pressures tried.		Propane 2.48 per cent. : Complete propagation at all pressures tried.	
Ethane 3.08 per cent. : Complete propagation not obtained at any pressure tried.		Propane 2.32 per cent. : Complete propagation not obtained at any pressure tried.	
(c) Butane.		(d) Pentane.	
Pressure. mm.	Limit. Per cent.	Pressure. mm.	Limit. Per cent.
760	1.92	760	1.75
970	1.89	1280	1.68
1430	1.86	1640	1.61
2460	1.86	1790	1.59
3150	1.89	2050	1.59
4330	1.92	3760	1.61
		4280	1.68
Butane 1.98 per cent. : Complete propagation at all pressures tried.		Pentane 1.75 per cent. : Complete propagation at all pressures tried.	
Butane 1.84 per cent. : Complete propagation not obtained at any pressure tried.		Pentane 1.54 per cent. : Complete propagation not obtained at any pressure tried.	

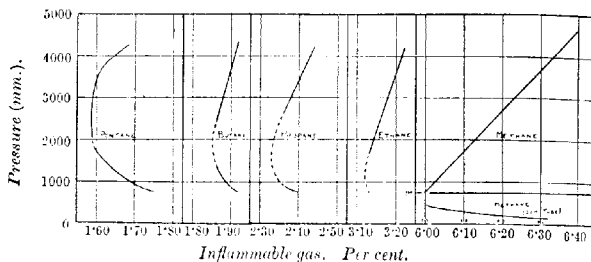
These results are shown diagrammatically in Fig. 1, together with those for methane previously determined. It will be seen that when the initial pressure of the mixture exceeds a certain value, which differs with each hydrocarbon, the lower limit is narrowed in each instance. With methane only is this critical pressure less than

atmospheric; and whilst, therefore, any increase in pressure above atmospheric at once increases the lower limit of methane, with the other hydrocarbons there is at first a slight extension of the limit. This extension is greatest with mixtures of pentane and air, with which it amounts to about 0.2 per cent. of pentane; and it continues until the initial pressure of the mixtures exceeds 3000 mm., after which the limit is narrowed.

The pressure at which narrowing of the lower limit occurs appears to be higher the higher is the molecular weight of the inflammable gas.

The upper limits were more sharply defined than the lower limits. The upper-limit mixtures of pentane and of butane with air deposited carbon when the initial pressure was atmospheric, as did the limit mixtures containing more of each inflammable gas at the higher

FIG. 1.



pressures. Limit mixtures of air with either propane or ethane did not deposit carbon when the initial pressure was atmospheric, but their limit mixtures at higher pressures did. The passage of flame in these upper-limit mixtures, more especially at the higher pressures, resulted in marked heating up of the walls of the glass tube, and it was necessary to allow a considerable time to elapse between each experiment for the tube to cool, or the results of the experiments were erratic. The carbon deposited on the sides of the tube did not appear to affect the results, but the tube was cleaned frequently between experiments with a mixture of concentrated sulphuric acid and sodium dichromate. The results obtained are recorded in Table II.

These results are shown diagrammatically in Fig. 2, the results for methane being included for comparison. The effect of increasing the initial pressure of the mixture on the upper limit is to widen it, and the effect is nearly the same with each of the paraffin hydrocarbons; their behaviour at the upper limit thus differs from that

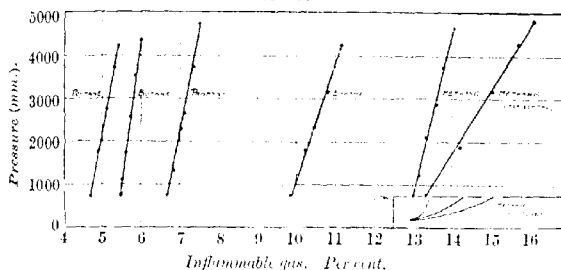
TABLE II.
Upper Limits.

Downward propagation of flame.

(a) Ethane.		(b) Propane.	
Pressure. mm.	Limit. Per cent.	Pressure. mm.	Limit. Per cent.
760	9.85	760	6.69
1220	10.05	1320	6.88
1850	10.25	2300	7.03
2360	10.45	2670	7.12
3190	10.80	3760	7.35
4280	11.16	4740	7.49

(c) Butane.		(d) Pentane.	
Pressure. mm.	Limit. Per cent.	Pressure. mm.	Limit. Per cent.
760	5.50	760	4.68
1120	5.54	1790	4.91
1790	5.65	2780	5.12
2570	5.75	3760	5.32
3550	5.87	4220	5.42
4380	6.00		

FIG. 2.



of hydrogen and carbon monoxide at both limits, and from their own behaviour at the lower limit.

The general tendency of increased initial pressure can be regarded as a tendency to shift the range of inflammability of each of the paraffin hydrocarbons. Thus with methane at atmospheric pressure the range of inflammability in air lies between 6.0 and 13.0 per cent. (downward propagation of flame). Under the same conditions of experiment, the range lies between 6.4 and 16.0 per cent. when the initial pressure of the mixtures is six atmospheres.

It has been shown (T., 1920, 117, 48) that if, for the sake of argument, the "flame-temperature" is assumed to be the same with all inflammable mixtures of methane and air, then, from the law of mass-action, the mixture in which the rate of reaction would be the fastest would contain 33.3 per cent. of methane. Since, however,

the "flame-temperature" varies according to the composition of the mixture, and is presumably at a maximum when the mixture contains the quantity of methane (9.45 per cent.) necessary for complete combustion, the most rapid rate of reaction and the fastest speed of uniform movement of flame are obtained with mixtures not far removed in composition from 9.45 per cent. of methane; whilst at ordinary temperatures and pressures a mixture of methane and air containing 33.3 per cent. of methane will not propagate flame.

The shifting of the range of inflammability as the initial pressure is increased would seem to indicate that the "flame-temperature," or, possibly, the lowest temperature at which flame begins to propagate, approaches a constant value over the whole range of mixtures as the initial pressure is increased. The shifting of the range of inflammability is in the direction one would expect if this reasoning is correct, not only with methane, but also with the other paraffin hydrocarbons.*

With mixtures of air with carbon monoxide and with hydrogen, the mixture in which the maximum rate of reaction would occur, according to the law of mass-action, would contain 66.6 per cent. of the inflammable gas (assuming, as before, that the flame-temperatures of all the mixtures were the same). Since the upper-limit mixture with both hydrogen and carbon monoxide contains more than 66.6 per cent. of inflammable gas, there is no movement of the range of inflammability and the limits are narrowed at both sides by increase of initial pressure.

Although this explanation would appear to be satisfactory so far as the widening of the upper limit of mixtures of methane (or other paraffin hydrocarbon) and air is concerned, there still remains to be explained the fact that the lower limit is narrowed. Since with each inflammable gas there is a limiting pressure below which no mixture of it with air will propagate flame, the first effect of increasing the pressure above this limiting pressure must be to widen the limits of inflammability at both sides. As the increase of pressure is continued, it is found that either or both of the limits may be narrowed. It has already been shown that the pressure at which this narrowing occurs on the lower-limit side differs with different inflammable gases; and there is no reason to doubt but that at considerably higher pressures than those employed in this research the upper limits (downward propagation of flame) of the paraffin hydrocarbons would be narrowed also.

* It is interesting to note in this connexion that Mason and Wheeler (*loc. cit.*) observed that when mixtures of methane and air were at an initial temperature greater than 600°, the range of inflammability was extended rapidly at the upper limit as the initial temperature was increased.

The explanation advanced by Terres and Plenz (*loc. cit.*) for the narrowing of the limits can only apply to downward propagation of flame. During the upward propagation of flame heat transferred by convection would not be lost, but would be utilised in raising the temperature of portions of the mixture about to be burnt.

Experiments to determine the limits of inflammability with upward propagation of flame, and with high initial pressures of the mixtures, have not been successful. An electric spark of high intensity has to be employed to ignite mixtures at high pressures, and such sparks produce large "caps" of flame in mixtures which are not capable of continued self-propagation of flame. These caps often extend throughout the length of the explosion tube and render it impossible to observe whether independent propagation of flame can take place or not.

Experiments in which the propagation of flame was horizontal were more successful and serve our purpose because, whether or not the flames in limit mixtures are assisted by convection currents during horizontal propagation, they are certainly not retarded by them. We can therefore judge from such experiments as to the validity of the suggestion of Terres and Plenz.

The lower limit of inflammability of methane in the apparatus used, horizontal propagation of flame, was 5.62 per cent. This mixture propagated flame at all pressures tried from 760 to 5000 mm. A mixture containing 5.56 per cent. of methane did not give complete propagation of flame at any pressure tried. The lower limit of inflammability of methane in air is therefore unaltered by variation in pressure between 760 and 5000 mm., when the flame propagates horizontally.

These results, and those at the upper limit, are recorded in Table III, and the latter are also shown diagrammatically in Fig. 2 for comparison with the results obtained when propagation of flame was downwards.

TABLE III

Lower Limit.

Horizontal propagation of flame.

Methane 5.62 per cent. : Complete propagation at all pressures tried.
 Methane 5.56 per cent. : Complete propagation not obtained at any pressure tried.

Upper Limit.

Horizontal propagation of flame.

Pressure. mm.	Limit. Per cent. methane.
760	13.31
1900	14.25
3190	15.02
4270	15.75
4900	16.12

It will be seen that the effect of pressure in extending the upper limit of inflammability of methane in air is more marked when the propagation of flame is horizontal than when it is downwards. These experiments confirm the suggestion of Terres and Plenz.

Experiments at Reduced Pressures.

Although the experimental method did not lend itself to a study of the effect of high initial pressures on the limits of inflammability when the propagation of flame is vertically upwards, a modification of the method enabled such observations to be made at comparatively low initial pressures, at all events as regards the upper limit; at the lower limit, upward propagation was masked by the production of large "caps" of flame above the spark used to effect ignition.

The apparatus used for these experiments consisted of a glass tube closed at both ends, 5 cm. in diameter and 50 cm. long. At one end platinum electrodes were fused and the other end was fitted with a tap, which made connexion with a gas-holder containing the mixture to be experimented with and an oil-pump for exhausting the tube before admitting the mixture. A mercury manometer was placed between the explosion vessel and the gas-holder.

The method of experiment, which was similar to that used for the experiments at high initial pressures, was to determine two pressures, differing by 10 mm., at the higher of which flame was found to propagate completely, whilst at the lower only partial propagation occurred. A series of sparks from a "10 inch" X-ray coil was used for igniting the mixtures. At very low pressures (about 90 mm. at the lower limit and 180 mm. at the upper limit) this source of ignition was not powerful enough to ignite mixtures which may possibly have been able to support independent propagation of flame had it once been started. With limit mixtures at pressure not too far removed from atmospheric, however, there was no doubt as to the correct limiting pressure, since a mixture which allowed of complete propagation of flame at that pressure only enabled flame to travel a few centimetres from the spark at a pressure 10 mm. lower. The results are recorded in Tables IV and V.

These results are shown diagrammatically in Fig. 3, and are in good agreement with those obtained at pressures above atmospheric, although they cannot be directly compared with them because the diameter of the tube was greater (5 cm. as compared with 2 cm.). The dotted lines in Fig. 3 extend the curves to include the results obtained at high pressures in the tube 2 cm. in diameter, on the assumption that the diameter of the tube has not affected the relative values.

TABLE IV.

Lower Limits.

(a) Downward propagation.

Methane. Per cent.	Limiting pressure. mm.	
	First limit.	Second limit.
5.75	Only partial propagation at all pressures tried.	
5.80	455	735
5.90	315	
5.99	270	
6.12	180	
6.48	(Complete propagation at 90 mm.) (No flame appeared at 80 mm.)	

(b) Horizontal propagation.

Methane. Per cent.	Limiting pressure. mm.	
5.39	760	
5.41	575	
5.51	380	
5.70	320	
5.75	285	
5.90	215	
6.12	120	
6.48	(Complete propagation at 90 mm.) (No flame appeared at 80 mm.)	

TABLE V.

Upper Limits.

(a) Downward propagation.

Methane. Per cent.	Limiting pressure. mm.	
13.38	760	
13.35	545	
13.23	330	
12.89	240	
12.21	(Complete propagation at 180 mm.) (No flame appeared at 170 mm.)	

(b) Horizontal propagation.

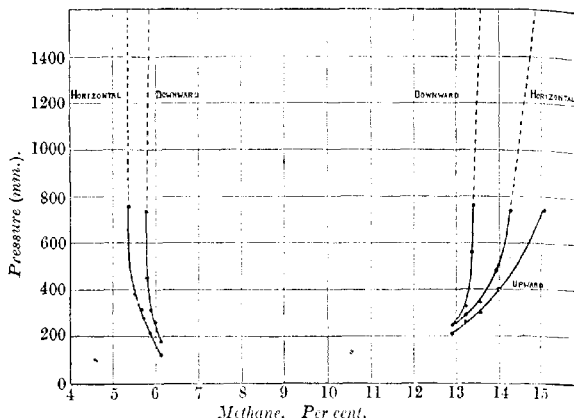
Methane. Per cent.	Limiting pressure. mm.	
15.11	745	
13.94	405	
13.59	300	
13.21	260	
12.89	210	
12.21	(Complete propagation at 160 mm.) (No flame appeared at 150 mm.)	

(c) Upward propagation.

Methane. Per cent.	Limiting pressure. mm.	
14.28	734	
13.94	485	
13.59	340	
13.23	290	
12.89	240	
12.21	(Complete propagation at 170 mm.) (No flame appeared at 160 mm.)	

Examination of these curves can leave no doubt but that the narrowing of the limits for downward propagation of flame under high pressures, when it occurs, is due to the action of convection currents, which must also affect the rate at which the limits widen with other modes of propagation. The fact that loss of heat by

FIG. 3.



convection is greatest at high pressures may be explained on the reasonable assumption that the transference depends on the difference of density of the hot and cold gases.

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[Received, January 31st, 1923.]

LV.—*Investigations on the Dependence of Rotatory Power on Chemical Constitution. Part XIX. The Rotatory and Refractive Dispersions and the Absorption Spectrum of d- γ -Nonyl Nitrite.*

By ROBERT HOWSON PICKARD and HAROLD HUNTER.

Rotatory Dispersion.

It has long been known that some connexion must exist between the rotatory dispersion of a substance and its absorption spectrum. Qualitative observations were recorded by Cotton (*Ann. Chim. Phys.*, 1896, [vii], 8, 373), who directed attention to the anomalous rotatory dispersion of the tartrates of chromium and copper in alkaline solution for light of wave-lengths approaching those of their absorption bands, whilst Grossmann and Loeb (*Z. physikal.*

Chem., 1910, 72, 93) observed similar phenomena in the cases of aqueous solutions of sugars and tartrates to which various coloured salts had been added. Like results were obtained by Becquerel (*Compt. rend.*, 1908, 147, 1281), who compared the rotatory dispersion and the absorption spectrum of well-formed crystals of cinnabar—possibly the most powerfully optically active substance known. Stewart, however, drew the conclusion (T., 1907, 91, 91, 1537) that no connexion could be found between the position of the absorption bands in the spectra of compounds and their rotatory powers, although he traced a parallelism between general absorptive power and rotatory power in the case of saturated and unsaturated acids, geometrical isomerides, homologous series, and active and racemic tartaric acids. More recently, Tschugaev and his co-workers (*Z. physikal. Chem.*, 1913, 45, 481, 553) have investigated this subject and have traced a general, but not a quantitative, relation between selective absorption and "abnormal" rotatory dispersion for derivatives of menthyl-, bornyl-, and fenchyl-xanthogenic esters.

During the last decade, however, a great deal of attention has been directed to the form of the rotatory dispersion curves of organic compounds, a field of research in which Lowry and his collaborators have been conspicuously active. Many forms of dispersion equation have been proposed, but the one adopted, both by Lowry and also in this series of investigations, is that proposed by Drude on theoretical grounds *—

$$\alpha = \sum \frac{k_0}{\lambda^2 - \lambda_0^2}$$

* The soundness of which has been, however, questioned by some mathematical physicists.

It is interesting to note that the earlier forms of dispersion equation which have been proposed and subsequently rejected as experimental tests became more stringent can all be derived as special cases of the Drude equation.

For, when $\lambda_0 = 0$, $\alpha = k/\lambda^2$ (Biot),
when $\lambda_0 < \lambda$, we may write—

$$\begin{aligned} \alpha &= \sum \frac{k_0}{\lambda^2 (1 - \frac{\lambda_0^2}{\lambda^2})} \\ &= \frac{\sum k_0}{\lambda^2} \left[1 + \frac{\sum \lambda_0^2}{\lambda^2} + \frac{\sum \lambda_0^4}{\lambda^4} + \dots \right] \end{aligned}$$

and then, if λ_0 is so much smaller than λ that the series is very rapidly convergent, we get the equation

$$\alpha = A/\lambda^2 + B/\lambda^4 \quad (\text{Boltzmann}),$$

from which, when λ_0 is smaller still, is derived—

$$\alpha = C + D/\lambda^2 \quad (\text{Stefan}).$$

Finally, when λ_0 is so small that we may write

$$1 - \lambda_0^2/\lambda^2 = (1 - \lambda_0^2/\lambda^2)^{\frac{1}{2}},$$

we get the equation due to Lommel.

By a similar treatment of the Sellmeier equation (p. 439), it is possible to derive the refractive dispersion equation proposed at an earlier date by Cauchy.

where k_0 , etc., are constants determining the magnitude of the rotatory power, and λ_0 , etc., are constants determining the form of the rotatory dispersion curve, and which correspond with wave-lengths of bands in the absorption spectrum of the substance.

From an exhaustive analysis of the results obtained by the study of the rotatory dispersion of nearly thirty secondary alcohols (Lowry, Pickard, and Kenyon, T., 1914, 105, 94), of α - and β -methyl glucosides (Lowry and Abram, *Trans. Faraday Soc.*, 1914, 10, 108), and especially of the data published by Rupe on the rotatory power of some forty compounds of the terpene series (Lowry and Abram, T., 1919, 115, 300), it has been shown that in most cases the simple Drude equation with one term, $\alpha = k_0/(\lambda^2 - \lambda_0^2)$, expresses the rotatory dispersion of these compounds with an accuracy which exceeds that attainable in any one set of polarimetric observations. Lowry has suggested, further, that in those cases where the one-term equation is insufficient to express the variation of rotatory power with wave-length, a two-term equation, $\alpha = k_0/(\lambda^2 - \lambda_0^2) + k_1/(\lambda^2 - \lambda_1^2)$, is amply sufficient to do so. This has been demonstrated in a most striking manner for ethyl tartrate by Lowry and Cutter (T., 1922, 121, 532) for light of thirty-six wave-lengths from $\lambda = 6708$ to $\lambda = 3860$ Å.U.

Whilst the agreement between the observed rotations and those calculated by means of a Drude equation is most satisfactory, it is nevertheless regrettable from one point of view that in most of the cases hitherto examined λ_0 has a value in the neighbourhood of 1600 Å.U., whilst in the case of ethyl tartrate (*loc. cit.*), the absorption bands predicted by the Drude equation would have wave-lengths of about 1700 and 2400 Å.U. That is to say, these bands have to be sought in a very remote and inaccessible region of the spectrum, where it would be very difficult to obtain direct experimental evidence of their existence. Even in the case of some derivatives of methylenecamphor (Lowry and Abram, T., 1919, 115, 300) with λ_0 at about 3000 Å.U., and of camphylcarbinol (*loc. cit.*) with λ_0 at about 3200 Å.U. no direct measurement of the actual positions of the bands has been made. Such experimental verification of the validity of the Drude equation is thus wanting, although its probability is increased by the agreement between the experimental and calculated figures, which, excellent as it is, yet leaves something to be desired when the very small fraction of the electromagnetic spectrum actually covered by the observed data is taken into account. In other words, λ_0 has hitherto of necessity been treated as an arbitrary constant and in fact Lowry and Abram (*loc. cit.*, p. 310) describe it as "hypothetical," whereas it is in reality a definite physical magnitude which is, or should be,

capable of measurement by methods entirely distinct from those of polarimetry.

If, therefore, an optically active compound can be obtained which exhibits selective absorption in a conveniently accessible region of the spectrum, it should be possible to predict the position of the absorption band from the Drude equation for rotatory dispersion: then this could be tested by direct measurement of its actual position, so that in this event the Drude equation would stand or fall by the agreement or divergence between prediction and observation. It is also desirable that this compound should be liquid in order that it may be examined polarimetrically in the homogeneous state, thus avoiding the complicating influence of solvents which conceivably would alter the value of λ_0 (compare, for example, Kazay, *Chem. Zentr.*, 1907, ii, 773).

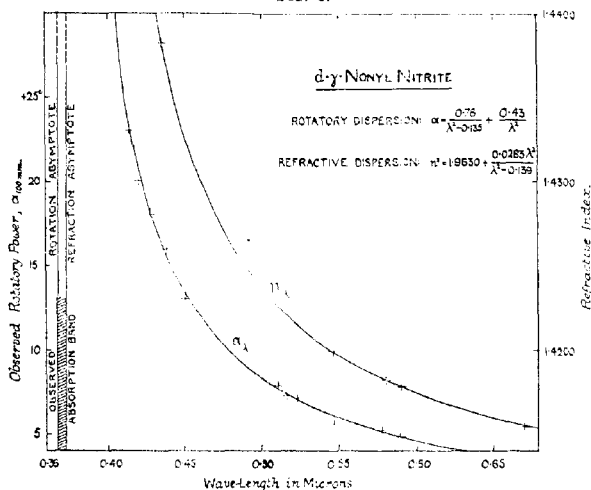
All these requirements are met by the nitrites of optically active alcohols of simple chemical constitution. In thick layers, the nitrite of *d*-ethyl-*n*-hexylcarbinol (γ -nonyl nitrite) is yellow, indicating absorption in the violet or very near ultra-violet. It is readily prepared in nearly quantitative yield by the action of gaseous nitrosyl chloride on a dry, ice-cold, pyridine solution of the appropriate alcohol.

On account of the experimental difficulties attendant on the polarimetric observations, the accuracy of the results is below that usually attained in this series of investigations, but it is considered advisable to publish them in their present form, as they have afforded such striking evidence in favour of the Drude equation. Although this compound in layers less than 0.05 cm. thick is transparent throughout the visible spectrum, it possesses a deep yellow colour in moderately thick layers and even with a column of liquid only 25 mm. thick it is difficult to read the polarimeter at $\lambda = 5105$ Å.U. The photographic observations are still more difficult to carry out. A layer of liquid only 3.9 mm. thick was employed, and even with this short column with an iron arc as illuminant and a half-shadow angle of 9° , it was found impossible to record observations on the more refrangible side of $\lambda = 4140$ Å.U. The observed (photographic) rotations thus had to be multiplied by 25 to obtain the values of $\alpha_{100\text{ mm.}}$, which cannot therefore be relied on to more than one unit. It has seemed best, therefore, to draw the rotatory dispersion curve (Fig. 1) for γ -nonyl nitrite which lay most evenly amongst the eleven experimental points and to calculate the constants of the Drude equation from this.

A one-term Drude equation was not sufficient to express the observed results. Considerable support is given to the view that this fact is due, not to the inaccuracy of the measurements, but

to a real complexity of rotatory dispersion by the fact that the next lower homologue, β -octyl nitrite, exhibits visibly anomalous rotatory dispersion and therefore must require a two-term dispersion equation with its terms differing in sign. As it would obviously be absurd to pretend to work out a four-constant equation with experimental figures of the accuracy attained in this investigation, the two-term Drude equation was reduced to a three-constant equation by neglecting λ_1 , a device which is quite allowable when dealing with rotations in the near neighbourhood of λ_0 , especially in the region on that side of λ_0 remote from λ_1 .

FIG. 1.



The calculated equation then takes the form

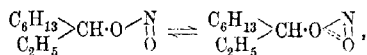
$$\alpha_{100 \text{ mm}} = \frac{0.76}{\lambda^2 - 0.135} + \frac{0.43}{\lambda^2}$$

where wave-lengths are measured in microns.

That is to say, this equation predicts an absorption band in the spectrum of γ -nonyl nitrite at $\lambda_0 = \sqrt{0.135}$, that is, at $\lambda_0 = 3680$ A.U. It is apparent, too, from the equation that although γ -nonyl nitrite exhibits complex rotatory dispersion, it cannot show anomalous rotatory dispersion of the type exhibited by ethyl tartrate in any region of the spectrum.

It is submitted that the cause of this complex rotatory dis-

person may be the existence within the apparently homogeneous liquid of two dynamic isomerides and that the composition of the nitrite may be represented by the equilibrium



although the possibility of the presence of associated molecules in the preparation must not be overlooked.

Refractive Dispersion.

It is somewhat surprising that, although a refractive dispersion equation,

$$n^2 = a^2 + \sum \frac{b_0 \lambda^2}{\lambda^2 - \lambda_0^2} \quad \dots \quad (i)$$

remarkable in its formal similarity to the Drude equation, was proposed more than fifty years ago by Sellmeier,* no attempt,† as far as is known to the authors of this paper, has been made by organic chemists to treat refractive dispersion in a manner analogous to rotatory dispersion. Refractive power has hitherto been studied without reference to the effect of dispersion, for the difference of refractive index for two standard wave-lengths is by no means a scientific measure of dispersion. It seems apparent that, when the multiplicity of formulæ for the calculation of refractive power, and the increase in the number of corrections for special effects such as ring closure, conjugation of double bonds, etc., are considered, existing methods are beginning to break down as the available experimental data become numerous and more accurate. Furthermore, it is noteworthy that those effects which complicate the calculation of refractive power, for example, conjugated systems of double bonds, the juxtaposition of ketonic groups, and the introduction into the molecule of elements of variable valency such as nitrogen and sulphur, are precisely those which characterise compounds which have absorption bands near to the visible spectrum. That is to say, the bands are nearer to the region of experimental observation and thus cause the effects of refractive dispersion to

* This equation generally bears Sellmeier's name, although it would appear that priority belongs to Maxwell, who proposed it in the form of a question set at the Cambridge Mathematical Tripos, 1869, two years before Sellmeier's work appeared.

† One example of its application to chemical problems is, however, to be found. Lübben has made measurements (*Ber. Deut. phys. Ges.*, 1914, 16, 180, 334) of the refractive dispersion of solutions of simple inorganic salts of the alkali metals and has succeeded in fitting this equation to his results, although he did not succeed in detecting the predicted absorption bands.

become more marked, with consequent disturbing effect on the refractive power calculated, as is common, with regard to one standard wave-length only, such as the sodium line, $\lambda = 5896$.

It seems therefore desirable that more attention should be directed to the form of the refractive dispersion curves of organic compounds in order that the effect of dispersion on refractive index may be studied and, if possible, eliminated in the investigation of refractive power. The Sellmeier equation appears to be a suitable one for this purpose, and it is at once obvious that the properties which render the alkyl nitrites so useful in testing the Drude equation will be equally useful when a test of the Sellmeier equation is contemplated. The form of the equation, however, may be modified slightly for our present purpose. In equation (i), n denotes the refractive index of the compound for light of wave-length λ , a^2 denotes its dielectric constant (specific inductive capacity), and λ_0 , etc., denote the wave-lengths of the absorption bands due to the electrons producing the dispersion.

It is proposed to call the constants " λ_0 ," etc., the "refractive dispersion constants" of the compound; and the constants " b_0 ," etc., its "refraction constants." If now we write the equation

$$n^2 = a^2 + \frac{b_0 \lambda^2}{\lambda^2 - \lambda_0^2} + \sum \frac{b_1 \lambda^2}{\lambda^2 - \lambda_1^2},$$

we may, at all events in the neighbourhood of the band at λ_0 , neglect λ_1 , etc., and the equation becomes

$$n^2 = a^2 + \frac{b_0 \lambda^2}{\lambda^2 - \lambda_0^2} + \sum \frac{b_1 \lambda^2}{\lambda^2} = \frac{b_0 \lambda^2}{\lambda^2 - \lambda_0^2} + c,$$

where c is a term which sums the numerical values of the dielectric constant and the refraction constants of the terms in which λ_1 , etc., have been neglected. We now have an equation involving three constants, of which two only are arbitrary—the third, λ_0 , is capable of measurement by other methods just as in the case of the Drude equation for rotatory dispersion.

The experimental work involved in this case is by no means difficult. Refractive indices were determined at 25° by means of a Pulfrich refractometer and may be considered accurate to 0.0002 unit. The refractive dispersion equation was calculated to be (with λ measured in microns as before)

$$n^2 = 1.9630 + 0.0283 \lambda^2 / (\lambda^2 - 0.139),$$

whence $\lambda_0 = \sqrt{0.139}$, that is, $\lambda_0 = 3730 \text{ \AA.U.}$

Table I shows the observed and calculated figures for the refractive index, and it will be noticed that the difference between these values is of the order of the experimental error.

TABLE I.

Refractive Dispersion of d- γ -Nonyl Nitrite.

λ (Å.U.).	$n_{\text{obsd.}}$	$n_{\text{calc.}}$	Difference.
6708	1.4153	1.4155	+ 0.0002
5896	1.4180	1.4179	-- 0.0001
5790	1.4184	1.4183	-- 0.0001
5461	1.4200	1.4199	-- 0.0001
4358	1.4384	1.4383	-- 0.0001

Absorption Spectrum.

The values for the wave-length of the dominant absorption band deduced from measurements of rotatory power and of refractive index are thus satisfactorily concordant. Experimental determination of the actual position of the band will now furnish evidence for or against the validity of the equations of Drude and Sellmeier. The intense colour of the compound renders difficult an accurate determination of the position of the head of the band in the homogeneous liquid condition, but by using a cell only 0.2 mm. thick it was found possible to fix the limits of the band at $\lambda_0 = 3670 - 3720$ Å.U.

It is therefore submitted that the very substantial agreement between the values obtained for the wave-length of the dominant band in the absorption spectrum of γ -nonyl nitrite—

(i) predicted from measurements of rotatory power, $\lambda_0 = 3680$ Å.U.;

(ii) predicted from measurements of refractive index, $\lambda_0 = 3730$ Å.U.;

(iii) by direct photographic measurement, $\lambda_0 = 3670-3720$ Å.U., furnishes strong evidence in support of the equations proposed for rotatory dispersion by Drude and for refractive dispersion by Sellmeier, and that it also furnishes evidence in favour of some connexion between refractive index and rotatory power such as was sought on theoretical grounds by Livers (Phil. Mag., 1913, [vi], 25, 817, *et seq.*) and experimentally by Peacock (I., 1914, 105, 2782; 1915, 107, 1547).

EXPERIMENTAL.

Preparation of Nitrosyl Chloride.—This was prepared by Tilden's method (T., 1860, 13, 630) of heating aqua regia and absorbing the nitrosyl chloride in concentrated sulphuric acid to form nitrosyl-sulphuric acid, from which nitrosyl chloride was subsequently regenerated by distillation with anhydrous sodium chloride. In order to avoid, as far as possible, contamination with hydrogen chloride, the nitrosyl chloride was condensed to a deep ruby red

liquid in a coil cooled to -20° in a mixture of ice and salt and then allowed to boil slowly into a solution of γ -nonanol.

Preparation of d- γ -Nonyl Nitrite, $C_6H_{13}\cdot CH_2\cdot O\cdot NO$.—Gaseous nitrosyl chloride was allowed to pass slowly into a dry solution of *d*- γ -nonanol (optically pure) in four times its weight of pyridine, the solution being well cooled in ice and salt. Pyridine hydrochloride was precipitated and the reaction mixture assumed a temporary green colour when saturation was complete. The mixture was kept over-night and then repeatedly washed with water, dilute hydrochloric acid, and finally with water to remove all traces of pyridine. Ether was added after the first washing to reduce loss of the ester during the washing operations. The ether solution was then dried over ignited potassium carbonate, the solvent removed, and the ester fractionally distilled under reduced pressure on the water-bath.

d- γ -Nonyl nitrite is a bright yellow, mobile liquid with a pleasant, nitrous ethereal smell. It boils at $83-84^{\circ}/24$ mm.

Determination of Rotatory Power.

Visual Measurements.—These measurements were made with a 25 mm. tube of liquid, using the sodium flame, the enclosed mercury arc, and the copper arc as illuminants. For the sodium flame and the mercury arc, a direct-vision spectroscopic eyepiece only was necessary to secure monochromatic illumination, but with the copper arc it was necessary to analyse the beam of light spectroscopically by means of a constant-deviation prism before it entered the polarimeter. The spectroscopic eyepiece was employed in addition in this case to give greater dispersion and to enable a wider slit to be used without sacrificing purity of illumination.

Photographic Measurements.—For these observations, the eyepiece of the polarimeter was removed and a long-focus combination substituted.* The polariser and half-shadow were turned through 90° so that the dividing line in the centre of the field was horizontal and then, by means of a condenser, a parallel beam of light from an iron arc was passed through the polarimeter to the object glass. It is essential to use parallel light in order to ensure equal illumination of both halves of the field even when the arc flickers. The long-focus objective was caused to throw an image of the field of the polarimeter on to the slit of a spectrograph consisting of a spectrometer with a single 60° dense glass prism and a quarter-plate folding camera fitted with a 16" box extension. With this apparatus the whole of the spectrum from $\lambda = 6000$ to

* These alterations were carried out in a most satisfactory manner by Messrs. Bellingham and Stanley, London.

$\lambda = 3550 \text{ \AA.U.}$ (the limit of transparency of the glass used) could be obtained on two quarter-plates, covering a length of about 8 inches. With it, too, the D lines could be distinctly resolved, whilst naturally the dispersion was considerably greater at the violet end. It was found utterly impossible to get blue light through a 25 mm. tube of liquid and, after many expedients, a parallel-sided glass trough, 3.9 mm. wide, was employed. Even then it was impossible to obtain readings within 400 \AA.U. of the head of the absorption band, although two-hour exposures on very fast plates (Imperial "Eclipse") were used. Difficulty was experienced, too, in deciding the exact position of extinction on the photographic negatives. The column of liquid causing rotation of the plane of polarisation was necessarily so short that, for any given setting of the polarimeter, several spectral lines on the plate appeared equally strong in both halves of the field and the only possible way of deciding on the true position of extinction was to take the mean of the two extreme positions where unequal intensity of the two halves of the field could first be definitely detected.

The observed rotations were measured at the laboratory temperature of $18-20^\circ$, and are given in Table II.

TABLE II.
Rotatory Dispersion of d- γ -Nonyl Nitrite.

λ (\AA.U.)	α , 3.9 mm.	α , 25 mm.	α , 100 mm.	
5893	—	$+1.21^\circ$	$+4.8^\circ$	Visual readings
5782	—	1.33	5.3	
5461	—	1.40	5.6	
5218	—	1.79	7.2	
5153	—	1.81	7.2	
5105	—	1.97	7.9	
4500	$+0.51$	—	13	Photographic readings
4384	0.62	—	16	
4272	0.70	—	18	
4200	0.80	—	20	
4144	0.91	—	23	

Determination of Refractive Index.

These measurements were made with a Pulfrich refractometer jacketed with water from a thermostat maintained at 20° . The experimental figures are quoted in the theoretical part.

Measurement of the Absorption Spectrum.

The spectrograph employed for this purpose was that used for measurements of rotatory power. As it was inadvisable to resort to dilution in order to obtain a narrow band, very narrow cells

had to be employed. Those finally adopted consisted of pieces of platinum foil about 2 cm. square with rectangular openings about 5 mm. by 10 mm. in one side. These pieces of metal were held between glass plates by means of two ordinary screw clips. This arrangement is very convenient because the cells can be filled by capillary attraction, they contain no soluble cement, are easily taken apart for cleaning, and can have their thickness accurately determined by means of a micrometer. Three cells were employed of thickness 0.2, 0.4, and 0.8 mm., respectively. Their disadvantage lies in the fact that it is difficult to keep them tight for organic liquids with low surface tensions, although even the thickest of them will keep tight to water for six hours or more. A hæmacytometer was used for a cell thickness of 0.1 mm. and, although in all cases the position of the band is distinct, its more refrangible edge is so near the limit of transparency of the glass apparatus employed that the photographs are not suitable for reproduction.

In conclusion, the authors wish to express their thanks to Dr. J. Kenyon for his valuable advice and help, and one of them wishes to acknowledge his indebtedness to the Department of Scientific and Industrial Research for a personal grant which has enabled this work to be carried out. Some of the materials used in the investigation were purchased from a grant made by the Government Grant Committee of the Royal Society.

BATTERSEA POLYTECHNIC, S.W. 11. [Received, February 14th, 1923.]

LVI.—*Researches on Residual Affinity and Coordination. Part XV. Interactions of Acetylpropionylmethane and the Tetrachlorides of Selenium and Tellurium.*

By GILBERT T. MORGAN and HARRY GORDON REEVES.

As the result of earlier investigations, an explanation has been advanced for the complicated changes occurring in the interactions of acetylacetone and the tetrachlorides of selenium and tellurium (T., 1920, **117**, 1456; 1921, **119**, 610; 1922, **121**, 922, 2432), but it remains to be seen whether this interpretation of experimental facts is consistent with the behaviour of other homologous aliphatic β -diketones when these are subjected to the action of the above-mentioned tetrachlorides. It is evident that each of these chlorides induces a characteristic tautomeric change in acetylacetone, this

alteration of chemical structure being manifested by the nature and constitution of the products.

Selenium tetrachloride removes from acetylacetone the two hydrogen atoms originally present in the methylene group of acetylacetone, yielding selenium acetylacetone, a non-enolic dimeric substance, $\text{Se}_2(\text{C}_5\text{H}_6\text{O}_2)_2$, the structural formula for which has been recently demonstrated (T., 1922, 121, 2432).

The reaction of tellurium tetrachloride and acetylacetone differed from that of selenium tetrachloride and the same β -diketone in its point of attack on the organic molecule and consequently in the chemical structures of the more numerous products, namely, tellurium acetylacetone dichloride, tellurium bisacetylacetone dichloride, and tellurium *O*-ethylacetylacetone trichloride, the last of these arising from the intervention of ethyl chloride present in chloroform B.P. (T., 1922, 121, 923). It is highly probable that the addition of tellurium to the diketonic chain is preceded by enolisation of acetylacetone into the modification $\text{CH}_3\text{CO}\cdot\text{CH}_2\cdot\text{C}(\text{OH})\cdot\text{CH}_3$, a reactive form of the substance capable of combining with tellurium tetrachloride to form the additive compound $\text{CH}_3\text{CO}\cdot\text{CH}_2\cdot\text{CCl}(\text{OH})\cdot\text{CH}_2\cdot\text{TeCl}_3$ (compare Bielecki and Henri, *Compt. rend.*, 1914, 158, 1922). This intermediate product by loss of hydrogen chloride furnishes a hypothetical substance, $\text{CH}_3\text{CO}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}_2\cdot\text{TeCl}_3$, from which the three foregoing stable tellurium compounds are derivable.

In view of these intricate chemical changes, it became of interest to study the behaviour of acetylpropionylmethane (propionylacetone), the next homologue of acetylacetone, towards the two tetrachlorides.

I. *Selenium Acetylpropionylmethane.*

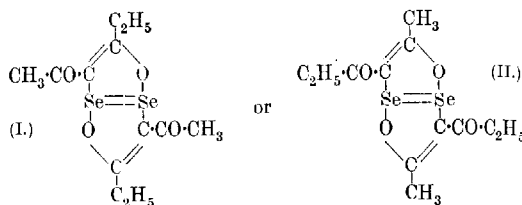
Towards selenium tetrachloride, acetylpropionylmethane reacts in a manner closely resembling acetylacetone. The condensation occurs most smoothly with the copper derivative of the diketone and there is only one seleniferous product, the non-enolic dimeric *selenium acetylpropionylmethane* (*selenium propionylacetone*; formula I or II), accompanied by *acetylpropionylechloromethane*, $\text{C}_5\text{H}_5\text{CO}\cdot\text{CHCl}\cdot\text{CO}\cdot\text{CH}_3$.

Selenium acetylpropionylmethane, an analogue of selenium acetylacetone, undergoes similar reactions with hydriodic and hydrocyanic acids and with excess of propionylacetone, the only practical difference being that the products are less stable, probably owing in part to their greater fusibility.

Diselenium bisacetylpropionylmethane, $\text{Se}_2\cdot(\text{C}_6\text{H}_8\text{O}\cdot\text{OH})_2$, obtained by the action of hydriodic acid, is a yellow oil identified by conversion into its yellow *copper* derivative, $\text{Se}_2\cdot(\text{C}_6\text{H}_8\text{O}\cdot\text{O})_2\cdot\text{Cu}$.

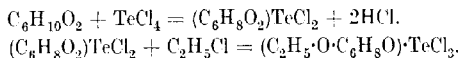
Cyano-3-selenium acetylpropionylmethane, $\text{CN}\cdot\text{Se}\cdot\text{C}_6\text{H}_8\text{O}\cdot\text{OH}$, a very fusible, colourless solid produced by the addition of hydrogen cyanide, is characterised by its crystalline *copper* derivative, $(\text{CN}\cdot\text{Se}\cdot\text{C}_6\text{H}_8\text{O}\cdot\text{O})_2\text{Cu}$.

Selenium OC-bisacetylpropionylmethane, $\text{O}\cdot\text{C}_6\text{H}_8\text{O}\cdot\text{Se}\cdot\text{C}_6\text{H}_8\text{O}\cdot\text{OH}$, arising from the addition of acetylpropionylmethane employed in excess, is an oil yielding a greenish-yellow copper salt.



II. Tellurium Acetylpropionylmethane.

The condensation of tellurium tetrachloride and acetylpropionylmethane proceeds more simply than in the case of acetylacetone. In this instance only one product is isolated, namely, *tellurium acetylpropionylmethane dichloride* (VII), which, however, on treatment with ethyl chloride in chloroform furnishes *tellurium O-ethylacetylpropionylmethane trichloride* (VIII).



The addition of tellurium tetrachloride to the methylene enolic form of acetylpropionylmethane takes place through the intermediate phases represented by formulae III, IV, and V, after which elimination of hydrogen chloride leads to tellurium acetylpropionylmethane dichloride (VII).* On treatment with sulphurous acid or alkali sulphites and bisulphites, the foregoing dichloride undergoes reduction to *tellurium acetylpropionylmethane* (VI), a well-defined, golden-yellow substance more soluble in water than its lower homologue, tellurium acetylacetone. The new product, which is of monomeric complexity, behaves as an unsaturated compound, combining additively with chlorine to regenerate the dichloride and

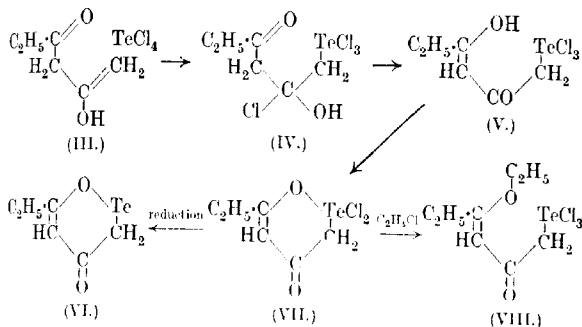
* The formulae for the tellurium compounds are based on the assumption that the preliminary change (VII) is an enolisation of the group $\text{CH}_3\text{CO}\cdot$, but there is an alternative possibility that this tautomeric rearrangement may have taken place in the group $\text{CH}_3\text{CH}_2\text{CO}$, thus giving rise to $\text{CH}_3\cdot\text{CH}(\text{C}(\text{OH}))$. These alternatives are presented in formulae I and II for the selenium derivative.

with bromine and iodine to form, respectively, tellurium acetylpropionylmethane dibromide and di-iodide.

Reference has already been made (T., 1922, 121, 940) to the intense germicidal action of aqueous solutions of tellurium acetylpropionylmethane, and the bacteriological and physiological study of this and other tellurium derivatives of the β -diketones is under investigation by Dr. E. A. Cooper. The following results show the disinfecting action of a series of these tellurium compounds.

B. Coli communis.

Substance.	Concentration disinfecting at 37°.	Phenol coefficient.
Tellurium acetylacetone	1 in 500,000	1,000
Tellurium 3-methylacetylacetone	1 in 800,000	1,600
Tellurium acetylpropionylmethane	1 in 2,500,000	5,000



Summary.

1. The lengthening of the β -diketone chain in passing from acetylacetone to its next homologue, acetylpropionylmethane, does not alter materially the nature of the interaction with selenium tetrachloride.

2. The condensation with tellurium tetrachloride is simplified in the case of acetylpropionylmethane, the only product isolated being tellurium acetylpropionylmethane dichloride.

EXPERIMENTAL.

I. *Selenium Series.*

Owing to the small yield of the starting material, acetylpropionylmethane (propionylacetone), obtained by the sodium ethoxide process the following modification was adopted. Forty-two c.c. of methyl ethyl ketone ($d = 0.9538$, 1 mol.) were added slowly and

with vigorous shaking to a mixture of 11 grams (1 atom) of clean sodium wire and 190 c.c. of dry redistilled ethyl acetate contained in a reflux apparatus cooled to 0° . After twelve hours, the mixture was heated on the water-bath for one and a half hours, cooled, and poured on to crushed ice. The ethereal layer was extracted twice with water, the combined aqueous layers neutralised with dilute acetic acid and treated with the calculated amount of $N/8$ -cupric acetate. The precipitated pale blue copper acetylpropionylmethane after washing with water was dried at 80° : m. p. $197-198^{\circ}$; yield 32.6 grams or 47.8 per cent. on the weight of methyl ethyl ketone.

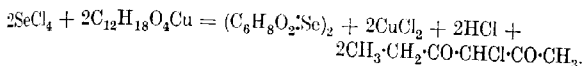
Acetylpropionylmethane (b. p. 158°) was obtained in almost quantitative yield by decomposing the copper salt with dilute sulphuric acid in presence of ether, the ethereal extract being fractionated after drying over sodium sulphate.

Selenium Acetylpropionylmethane (Selenium Propionylacetone) (Formulae I and II).—Copper acetylpropionylmethane (10.2 grams, 1 mol.) was added slowly with shaking to 7.8 grams of freshly prepared selenium tetrachloride, suspended in 56 c.c. of chloroform B.P., care being taken to exclude moisture. Hydrogen chloride was evolved, the solution reddened, and the tetrachloride gradually dissolved while cupric chloride (5 grams) with a trace of selenium was precipitated. After thirty minutes at the ordinary temperature, this deposit was removed and the deep red, fuming, lachrymatory filtrate was evaporated rapidly in a current of air, when the residue, a reddish-brown oil, solidified almost completely and on trituration with absolute alcohol yielded yellow, crystalline *selenium acetylpropionylmethane* (yield 24.5 per cent.). Recrystallised from absolute alcohol, this product separated in pale yellow, glistening plates melting at 137° ; its solution in benzene or alcohol had a yellow colour; it was only faintly acid to litmus and dissolved in aqueous sodium hydroxide to a yellow solution, gradually decomposing with precipitation of selenium [Found: C = 37.62; H = 4.41; Se = 41.12. $C_{12}H_{16}O_4Se_2$ requires C = 37.66; H = 4.22; Se = 41.40 per cent. An ebullioscopic molecular weight determination in benzene ($c = 2.17$) gave $M = 372$. $(C_{12}H_{16}O_4Se)_2$ requires $M = 382.6$.]

Selenium acetylpropionylmethane was practically insoluble in water or ether; it yielded selenium on warming with alcoholic aniline and became superficially coated with red selenium on exposure to light.

3-Acetylpropionylchloromethane, copper salt.—The alcohol employed in assisting the initial crystallisation of crude selenium acetylpropionylmethane was evaporated in a current of air, leaving a residue of red lachrymatory oil and a supernatant layer of hydro-

chloric acid. An ethereal solution of the oil, when shaken with aqueous copper acetate, yielded a yellowish-green, granular precipitate of *copper 3-acetylpropionylchloromethane*, $\text{Cu}(\text{C}_6\text{H}_8\text{O}_2\text{Cl})_2$, which crystallised from chloroform in olive-green plates melting at $137-138^\circ$ (Found: Cl = 19.66; Cu = 17.44. $\text{C}_{12}\text{H}_{18}\text{O}_4\text{Cl}_2\text{Cu}$ requires Cl = 19.76; Cu = 17.72 per cent.). This result confirmed the following equation representing the formation of selenium acetylpropionylmethane:



Diselenium Bisacetylpropionylmethane, $\text{Se}_2(\text{C}_6\text{H}_8\text{O}\cdot\text{O})_2$.—Two molecular proportions (0.63 gram) of 60 per cent. hydriodic acid diluted with 40 c.c. of water were added to 0.9 gram of selenium acetylpropionylmethane (1 mol.) suspended in 150 c.c. of ether cooled by adding 1 gram of crushed ice, the mixture being shaken vigorously. The brown colour of the ethereal layer due to iodine was removed by adding N/10-thiosulphate, the decolorised solution dried over sodium sulphate, and the ether removed in a vacuum. The residual yellow oil (0.4 gram, 42 per cent.) would not solidify but had the characteristic offensive odour of the diselenium bis- β -diketones (Morgan, Drew, and Barker, *loc. cit.*). It contained Se = 41.93. $\text{C}_{12}\text{H}_{18}\text{O}_4\text{Se}_2$ requires Se = 41.13 per cent. On shaking with ether and cupric acetate, it readily yielded a mustard yellow *copper salt*, $\text{Se}_2(\text{C}_6\text{H}_8\text{O}\cdot\text{O})_2\cdot\text{Cu}$ (Found: C = 31.98; H = 3.98. $\text{C}_{12}\text{H}_{16}\text{O}_4\text{Se}_2\text{Cu}$ requires C = 32.30; H = 3.62 per cent.).

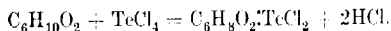
Cyano-3-selenium Acetylpropionylmethane, $\text{CN}\cdot\text{Se}\cdot\text{C}_6\text{H}_8\text{O}\cdot\text{OH}$.—One gram of powdered selenium acetylpropionylmethane dissolved in four or five minutes to a pale yellow solution when shaken with 6 c.c. of redistilled hydrogen cyanide and 12 c.c. of dry ether. After removing the volatile constituents of the solution in a vacuum, a mass of flat, six-sided needles was obtained melting at 27.5° . These crystals, which had a distinct odour of burnt rubber similar to that of the other cyanoselenium derivatives, liquefied on keeping for a short time to a yellow oil which did not solidify again on cooling. Both the oil and the original crystals gave a red ferric chloride coloration. Owing to this instability the crystalline cyano-derivative was converted into *copper salt*, $(\text{CN}\cdot\text{Se}\cdot\text{C}_6\text{H}_8\text{O}\cdot\text{O})_2\text{Cu}$, by dissolving in ether and shaking with aqueous cupric acetate. The well-defined, crystalline, pale blue copper derivative (yield 70 per cent.), which gradually decomposed on keeping, was readily soluble in chloroform (Found: N = 5.67; Se = 31.3; Cu = 12.2. $\text{C}_{12}\text{H}_{14}\text{O}_4\text{N}_2\text{Se}_2\text{Cu}$ requires N = 5.62; Se = 31.84; Cu = 12.76 per cent.).

Selenium OC-bisacetylpropionylmethane, $\text{Se} < \begin{smallmatrix} \text{C}_6\text{H}_8\text{O}\cdot\text{OH} \\ \text{O}\cdot\text{C}_6\text{H}_8\text{O} \end{smallmatrix}$, was obtained as an oil which could not be induced to crystallise on refluxing 1 gram of powdered selenium acetylpropionylmethane, 2 grams of acetylpropionylmethane, and 14 c.c. of chloroform, a trace of solid sodium hydroxide being added as catalyst. After ten to fifteen minutes, the solution assumed a pink tint owing to a slight elimination of selenium; the chloroform and excess of β -diketone were removed in a vacuum over sodium hydroxide. The residual oily selenium bisacetylpropionylmethane, which had the characteristic odour of burnt rubber, was readily soluble in chloroform but only sparingly soluble in petroleum. On shaking its warm petroleum solution with aqueous cupric acetate, the greenish-yellow *copper* salt was obtained, which gave analytical numbers approximating to the formula $(\text{C}_{12}\text{H}_{17}\text{O}_4\text{Se})_2\text{Cu}$.

II. Tellurium Series.

Tellurium Acetylpropionylmethane Dichloride (Formula VII).—Acetylpropionylmethane (3.54 grams, 2 mols.) and 3 grams of sublimed tellurium tetrachloride (1 mol.), suspended in 24 c.c. of chloroform B.P., were heated under reflux for one and a half hours, when the evolution of hydrogen chloride had ceased. The yellow filtrate from a slight deposit of tellurium was concentrated in a vacuum desiccator over lime until three crops of *tellurium acetylpropionylmethane dichloride* were obtained (total 2.2 grams). This dichloride was almost insoluble in water, but dissolved sparingly in ether, benzene, or chloroform and very readily in cold acetone, from which solvent it crystallised slowly in large, transparent prisms melting with decomposition at $170\text{--}171^\circ$. When recrystallised from hot alcohol, the substance was obtained in white nodules becoming discoloured at 175° and changing to a black mass at 185° (Found: Cl = 22.89; Te = 40.94. $\text{C}_6\text{H}_8\text{O}_2\text{Cl}_2\text{Te}$ requires Cl = 22.83; Te = 41.01 per cent.).

Tellurium acetylpropionylmethane dichloride resembled closely its isomeride, tellurium 3-methylacetylacetone dichloride (T., 192^a, *loc. cit.*); on keeping for some time, it became brownish-grey owing to slight decomposition with elimination of tellurium. On repeating the foregoing preparation in pure "salicylide" chloroform, no other product than the dichloride was observed:



Tellurium Acetylpropionylmethane (Formula VI).—Powdered potassium metabisulphite (2.8 grams \equiv 4 mols. KHSO_3) was added during ten minutes to a well-stirred suspension of 2 grams of tellurium acetylpropionylmethane dichloride in 40 c.c. of ice-cold water.

Sulphur dioxide was evolved, the dichloride dissolved to a golden-yellow solution, and after removing a slight deposit of tellurium the filtrate was concentrated until well-defined, golden-yellow, acicular prisms separated. This product was recrystallised from hot benzene and obtained in golden-yellow needles melting at 100° (1.2 grams, yield 79 per cent.) [Found: C = 29.85; H = 3.66; Te = 53.00. $C_6H_8O_2Te$ requires C = 30.06; H = 3.36; Te = 53.24 per cent. An ebullioscopic determination of molecular weight in benzene ($c = 0.85$) gave $M = 233$. $C_6H_8O_2Te$ requires $M = 239.6$]. The foregoing reduction was also readily accomplished by means of sodium sulphite, but with a somewhat decreased yield. Tellurium acetylpropionylmethane was much more soluble in water than in organic media, but fairly soluble in cold benzene or chloroform. Its aqueous solution, which slowly deposited tellurium, has been employed in bacteriological work, showing the highest germicidal activity of its series of tellurium derivatives (T., 1922, *loc. cit.*).

Tellurium acetylpropionylmethane dibromide, $C_6H_8O_2TeBr_2$, prepared by mixing tellurium acetylpropionylmethane and bromine in chloroform solution, separated in pale yellow nodules, and when crystallised from hot alcohol was obtained in white prisms melting and decomposing at 156° (Found: Br = 40.39. $C_6H_8O_2Br_2Te$ requires Br = 40.00 per cent.).

Tellurium acetylpropionylmethane di-iodide, $C_6H_8O_2TeI_2$, was obtained as crimson needles and in quantitative yield from its generators in chloroform solution; it crystallised from hot alcohol in reddish-purple needles; the lighter variety sintered at 130° and intumescend at 190° , the darker form sintered at 135° and intumescend at 185° (Found: I = 51.33. $C_6H_8O_2I_2Te$ requires I = 51.43 per cent.).

Tellurium O-Ethylacetylpropionylmethane Trichloride (Formula VIII).—Powdered tellurium acetylpropionylmethane dichloride (1.5 grams) was added to 2.5 c.c. of chloroform B.P. saturated with hydrogen chloride, 3 c.c. of ethyl chloride were added, and the yellow solution was heated under reflux for two hours. On cooling, a small amount of tellurium dioxide was precipitated, and the brownish-yellow filtrate concentrated in a vacuum over lime. The yellowish-brown, oily residue solidified completely to a crystalline, yellowish-white solid, which was extracted with cold chloroform. The filtered extract, when concentrated under reduced pressure, yielded a buff-coloured, crystalline solid, which was redissolved in chloroform and precipitated by light petroleum. It then separated in pale yellow, prismatic needles commencing to change at 112° and decomposing at 120° (Found: Cl = 28.50; Te = 34.12. $C_6H_{11}O_2Cl_3Te$ requires Cl = 28.30; Te = 33.91 per cent.).

Tellurium O-ethylacetylpropionylmethane trichloride slowly became brownish-grey owing to elimination of traces of tellurium. Dissolved in chloroform, it developed no red coloration with alcoholic ferric chloride; however, on boiling and leaving over-night, a deep red coloration developed. On treatment with aqueous sodium hydroxide, the trichloride underwent destructive hydrolysis, gave a greenish-yellow solution, and evolved a characteristic earthy odour of the *O*-ethyl ether of acetylpropionylmethane.

The authors desire to express their thanks to the Advisory Council of the Department of Scientific and Industrial Research for grants which have partly defrayed the expenses of this investigation.

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[Received, December 13th, 1922.]

LVII.—*The Adsorption of Stannous Chloride by Stannic Acid.*

By GEORGE ERNEST COLLINS and JOHN KERFOOT WOOD.

ONE of the reactions of stannic acid which has from time to time attracted attention is that which takes place on the addition of a solution of stannous chloride. Under such conditions, a yellow or yellowish-brown precipitate is obtained, the composition of which, according to the analyses of Frémy (*Ann. Chim. Phys.*, 1848, [iii], 23, 393), Schiff (*Annalen*, 1861, 120, 47), and Tschermak (*J. pr. Chem.*, 1862, 86, 334), appears to vary to a certain degree according to the character of the stannic acid employed. It was observed by Löwenthal (*J. pr. Chem.*, 1859, 77, 321), Biron (*J. Russ. Phys. Chem. Soc.*, 1905, 37, 963), and others that no coloration or precipitate is obtained if stannous chloride is added to a freshly prepared, moderately concentrated solution of stannic chloride or sulphate, but that after some time, depending on the concentration of the solution, a coloration or precipitate begins to develop. This is explained by the gradual formation of stannic hydroxide as a result of the hydrolysis of the stannic salt, the hydroxide so produced then reacting with the stannous chloride. Any condition which tends to prevent the hydrolysis, as, for example, the simultaneous presence of a tartrate or an oxalate, causes the reaction to fail. Arising out of this behaviour of stannic salts, Löwenthal expressed the opinion that the stannous chloride reaction is not given by α -stannic acid, but is only obtained when the acid has acquired a β -character. Evidence on this point appears to be of a

contradictory nature; it will, however, be readily recognised from what has been stated in former papers by the present authors (T., 1922, 121, 441, 1122) that it is practically impossible to put the matter to a direct test owing to the fact that α -stannic acid begins, as soon as it is produced, to undergo condensation so that a product of more or less β -character is always obtained.

The variation in the composition of the precipitate suggests that it may be an adsorption product and not a true compound. Assuming this to be the case, it should be possible to obtain an isotherm of the ordinary character, and no matter how small the original concentration of stannous chloride was, some of the salt should always be left in solution. Frémy stated that by the use of a sufficient quantity of stannic acid it was possible to remove the whole of the stannous salt from solution, but this was disputed by Tschermak. The experiments made by the authors show that with different modifications of stannic acid adsorption isotherms of the ordinary type are obtained and that some stannous compound always remains unadsorbed, although the amount is very small when solutions of low concentration are used. The authors have also shown that both constituents of the stannous chloride are adsorbed by the stannic acid, although the concentration of the two elements in the solution is not reduced in the same proportion, a larger relative amount of tin than of chlorine being taken up. Probably a portion of the tin is adsorbed in the condition of stannous chloride and the remainder as stannous hydroxide.

In accordance with the authors' theory respecting the isomerism of the stannic acids, it would be anticipated that the greater the extent to which the process of condensation takes place the greater will be the reduction in the surface of the acid. From this point of view, therefore, an acid of pronounced β -character should have a smaller adsorptive power than would be possessed by a sample of acid in which the α - β -change had progressed to a lesser degree. The authors' results showed, however, that when the behaviour of equivalent amounts of two modifications of stannic acid was compared, the sample of the more pronounced β -character had the rather greater adsorptive power. It would therefore appear probable that the amount of adsorption is not governed entirely by the size of the grains of stannic acid, but that some other factor is involved; Löwenthal's view that the stannous chloride reaction is given only by β -stannic acid is in harmony with the comparative behaviour of the two samples of stannic acid employed.

The adsorption product contains tin in two states of oxidation and might, perhaps, be regarded as a stannous salt of stannic

acid. Such a salt would suffer a certain amount of decomposition in the presence of hydrochloric acid, whilst the stannic acid would tend to be resolved into modifications of a lesser degree of condensation, and possessing, as indicated previously, a lower adsorptive power for stannous chloride. As a consequence of these changes, the adsorptive power of stannic acid for stannous chloride should be smaller in the presence of hydrochloric acid. This anticipation was borne out by the results of experiments carried out by the authors under such conditions.

EXPERIMENTAL.

The α - and β -stannic acids employed were prepared by the methods described in a previous paper (T., 1922, 121, 1122).

In order to avoid the hydrolytic decomposition which always occurs when stannous chloride is dissolved in water, an alcoholic solution of the salt was prepared and filtered; solutions of varying degrees of concentration were then made up by diluting the clear filtrate with alcohol (90 per cent.).

Twenty-five c.c. of the various solutions were shaken each with an amount of stannic acid corresponding with 30 millimols. of stannic oxide. A brownish-yellow product was immediately formed and, after being again shaken once or twice, the mixtures were kept for about two hours at the temperature of the laboratory in order to ensure complete adsorption and to permit of the settling of the solid. Portions of the clear supernatant solutions were then removed and the amount of tin in the stannous condition estimated by titration with iodine in an atmosphere of carbon dioxide; the initial concentration of the various solutions being known, the amount of adsorption could be readily calculated. The results obtained are shown in the following tables.

Adsorption of Stannous Chloride.

By α -stannic acid.				By β -stannic acid.			
Millimols. of SnO in 25 c.c. of soln. before adsorp- tion.	Millimols. of SnO adsorbed.		Gram.-mols. of SnO per litre after adsorp- tion.	Millimols. of SnO in 25 c.c. of soln. before adsorp- tion.	Millimols. of SnO adsorbed.		Gram.-mols. of SnO per litre after adsorp- tion.
	Found.	Calc.			Found.	Calc.	
32.1	5.9	5.96	1.05	17.0	5.5	5.55	0.46
26.4	5.7	5.62	0.83	9.6	4.4	4.69	0.21
20.9	5.3	5.24	0.62	6.1	3.9	3.89	0.088
13.0	4.3	4.56	0.35	3.8	3.1	2.99	0.026
5.3	3.3	3.20	0.08	2.5	2.3	2.30	0.0077
2.2	1.95	1.91	0.01				
1.05	0.96	1.18	0.0036				

On plotting the experimental results, adsorption isotherms of the ordinary type are obtained. Each of the curves may be represented by the equation $a = kc^{1/n}$, where a represents the amount of stannous oxide adsorbed and c the concentration of the solution on the attainment of equilibrium. In the case of α -stannic acid, $n = 4.1$ and $k = 5.89$, whilst for the β -acid the values are $n = 4.65$ and $k = 6.56$. It will be seen from the table that the amount of stannous oxide adsorbed is in most cases in good agreement with the quantity calculated from the concentration of the solution by the use of the equations given above.

It is not evident from the adsorption experiments as described whether the tin is adsorbed in the condition of stannous chloride or of stannous hydroxide; experiments were therefore made to gain information on this point. In the event of the tin being adsorbed as hydroxide the volume of alkali necessary to render the solution alkaline should be the same before and after adsorption, whilst in the event of chlorine as well as tin being adsorbed the volume of alkali necessary for imparting an alkaline reaction would be diminished. Two solutions, of different concentrations, of stannous chloride in alcohol were prepared and to equal volumes of these equal weights of β -stannic acid were added. Equal volumes of each of the solutions were titrated before and after adsorption by solutions of iodine and potassium hydroxide, methyl-orange being employed as indicator with the latter. The following results were obtained:

	Iodine titres.			Potash titres.		
	Before.	After.	Percentage diminution.	Before.	After.	Percentage diminution.
Soln. A	13.2	3.2	76	23.0	12.1	47
Soln. B	6.1	0.1	98	10.0	2.0	80

It is obvious, therefore, that both elements are adsorbed, but that a larger proportion of tin than of chlorine is taken up. The most probable explanation is that a portion of the tin is adsorbed as stannous hydroxide.

Influence of Hydrochloric Acid on the Adsorption of Stannous Chloride by Stannic Acid.—An alcoholic solution of stannous chloride was acidified with hydrochloric acid to avoid subsequent hydrolysis. To three portions (25 c.c.) of the acid liquid were respectively added 10 c.c. of water, 5 c.c. of water and 5 c.c. of hydrochloric acid (3.88*N*), and 10 c.c. of hydrochloric acid (3.88*N*). To each of the mixtures 5 grams of a sample of β -stannic acid were added; the mixtures were well shaken, and after three hours the unadsorbed stannous compound was estimated by means of iodine. The results obtained are shown in the following table, the original

concentration of the stannous chloride and the amount adsorbed being expressed in terms of the iodine solution employed.

Adsorption of Stannous Chloride in presence of Hydrochloric Acid.

Composition of mixture.	Original titre.	Final titre.	Amount adsorbed.	Colour of precipitate.
A. 25 c.c. of SnCl_2 } 10 c.c. of H_2O }	28.5	13.9	14.6	Brownish-yellow
B. 25 c.c. of SnCl_2 } 5 c.c. of H_2O } 5 c.c. of HCl }	28.5	15.8	12.7	{ Intermediate be. tween those of A and C.
C. 25 c.c. of SnCl_2 } 10 c.c. of HCl }	28.5	17.5	11.0	
				Greenish-yellow.

The influence of the hydrochloric acid in reducing the amount of adsorption is shown by the above figures. It will also be noticed that the colour of the precipitate is somewhat modified by the amount of acid present in the mixture.

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[Received, November 16th, 1922.]

LVIII.—*Studies on Metal Hydrides. The Electrolytic Formation of Stibine in Sulphuric Acid and in Sodium Hydroxide Solution.*

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STANLEY WILSON WORRELL.

THE electrolytic formation of metal hydrides either of a chemical or of a more physical nature is a matter of considerable importance. In some cases electrolytically deposited metals contain hydrogen, in others, such as in that of bismuth, the physical condition of the deposited metal is found to depend almost wholly on whether the conditions have been such that the intermediate formation of a hydride was possible or not (Sand, T., 1907, 91, 384).

It has been known for some time that hydrides may be prepared from various elements by the action of nascent electrolytic hydrogen. The fact that hydrogen liberated from an antimony cathode contains a considerable percentage of stibine is mentioned by Newbery (T., 1916, 109, 1361) and the utilisation of this circumstance for the preparative production of stibine has been recently advocated by Paneth (*Z. Elektrochem.*, 1920, 26, 453) in a well-known paper, in which references to the electrolytic preparation of other hydrides may be found. .

The present paper deals with the conditions under which stibine

is formed when hydrogen is generated on an antimony cathode in solutions of sulphuric acid and sodium hydroxide. The points to which attention has been more particularly directed are, the dependence of yield of stibine on overvoltage, current density, temperature, and concentration of the electrolyte.

EXPERIMENTAL.

Overvoltage.—For the measurement of overvoltage at varying current densities, two distinct methods are in use, and some controversy regarding their relative merits has taken place (MacInnes, *J. Amer. Chem. Soc.*, 1919, **41**, 2013; 1920, **42**, 2233; Newbery, *ibid.*, p. 2007; Dunhill, T., 1921, **119**, 1081; Newbery, *ibid.*, 1922, **121**, 7; Tartar and Keyes, *J. Amer. Chem. Soc.*, 1922, **44**, 557). According to the first method, a connexion is tapped off from the liquid in the immediate vicinity of the working electrode to an auxiliary electrode, and the potential between the two electrodes is measured during the passage of the current. This method yields the sum of the "polarisation" and the "transfer-resistance" of the electrode. The importance of transfer-resistance was first pointed out by Gore in 1885. It represents a quantity which depends very greatly on conditions in the electrolyte difficult to control, and is of more physical than chemical interest (Sand and Black, *Z. physikal. Chem.*, 1909, **70**, 496; Newbery, *Trans. Faraday Soc.*, 1919, **15**, 126). The second method measures only the "polarisation" and its results are therefore of more direct chemical interest. It consists in allowing the working electrode to be connected alternately with great rapidity to the source of current and to a connexion leading through a potentiometer to an auxiliary electrode. The method is an old one. The devices employed in the past for effecting the change of connexion generally consisted of tuning forks and various forms of electromagnetic interrupters. In more recent years, rotary commutators have been employed with considerable success by Pring and Tainton (T., 1914, **105**, 721) and Newbery (T., 1914, **105**, 2419; 1916, **109**, 1105; 1917, **111**, 470; 1921, **119**, 477). For the purposes of the present research, both methods were tried, and in agreement with the explanation given, the results obtained by the first method were variable, whereas quite definite results were obtained by the second, provided that the speed of the commutator was sufficiently great. The first method was therefore definitely abandoned in favour of the second.

Determination of the Yield of Stibine.—The gas generated at the antimony cathode consisted of a mixture of hydrogen and stibine. It is known that stibine is catalytically decomposed into its elements by concentrated acid and by alkali. In agreement with this, it

was found that in 8*N*-sulphuric acid all the stibine that had been originally formed could not be collected as such, since a proportion varying from about 35 per cent. at 0° to about 54 per cent. at 80° had been decomposed. This was recognised by the fact that a precipitate of finely divided antimony was present in the liquid. It was filtered off, dried with alcohol and ether, and weighed. The filtrate was tested for antimony, but only negligible traces were found. In the experiments on alkaline solutions, only about one-tenth of the stibine usually passed off as gas, the rest was found decomposed. To estimate the stibine in the gaseous mixture, it was passed first through a trap for condensing water, then through a calcium chloride tube to dry it thoroughly, and then through a Geissler absorption tube containing *N*/10-silver nitrate, where the stibine was completely decomposed according to the equation



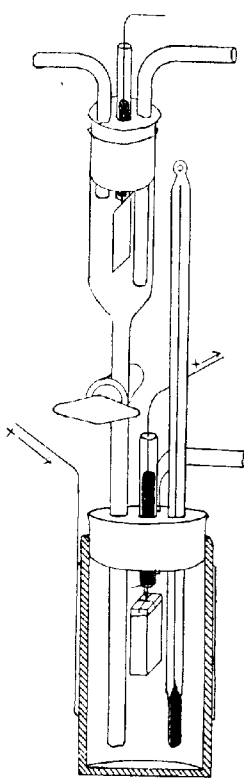
Any subsequent interaction between the silver nitrate and the silver antimonide would not affect the weight of the bulb (Reckleben, *Ber.*, 1909, 42, 1438). The completeness of the decomposition was inferred from the fact that the last bulb of the absorption apparatus always remained quite clear and colourless. After leaving the Geissler absorption vessel, the gas passed through two further calcium chloride tubes for retaining the water vapour carried over from the silver nitrate solution. The increase of weight of the Geissler bulb plus that of the first calcium chloride tube thus gave the weight of the stibine decomposed. The weight of the second calcium chloride tube, as well as of that before the Geissler apparatus, was always found unchanged. The gas then passed into a nitrometer, where it was measured. Before starting an experiment, the apparatus was filled with hydrogen. At the end of each experiment all the stibine was swept through the absorption vessels by means of hydrogen, which was later displaced by air. The amount of electrolytic hydrogen collected in an experiment was about 200 c.c. In the case of 8*N*-sulphuric acid, and in that of the alkaline solutions, the amount of stibine was calculated that corresponded with the antimony precipitated in the liquid, and this was added to the stibine which had been decomposed by the silver nitrate. Similarly, the hydrogen derived from this stibine was subtracted from that measured in the nitrometer. The yields are calculated so as to express the percentage ratio of the total volume of stibine to the volume of hydrogen plus stibine. The numbers thus represent the ratio of molecules of stibine to total number of molecules generated at the cathode. That the antimony precipitated in the strongly acid and in the alkaline

solutions was derived from the stibine primarily formed could also be inferred from the fact that when the yield of stibine corresponding with this antimony plus the gas decomposed by the silver nitrate was determined, perfectly definite and regular results were obtained, whereas the yields of stibine determined by the silver nitrate alone were variable and irregular.

Apparatus.—Fig. 1 represents the cathode compartment of the electrolytic vessel surrounded by the anode. It consists of a pot of porous earthenware closed by a rubber stopper. The anode was a piece of platinum foil completely surrounding the pot in the experiments with an acid electrolyte, and a similar piece of nickel gauze when the electrolyte was alkaline. Through the rubber stopper passed a thermometer, a glass tube holding the mercury platinum-wire connexion to the cathode, the stem of a tap funnel, and the exit tube for the mixture of hydrogen and stibine. The cathode was a stick of Kahlbaum's purest antimony of rectangular section dating from 1909. The principal dimensions of the piece used in the experiments on acid electrolytes were 0.6, 1.3, and 2.25 cm., corresponding with a surface of 10.11 sq. cm.; in the experiments on alkaline electrolytes the dimensions were 2.2, 1.3, and 0.6 cm., corresponding with a surface of 9.92 sq. cm. The antimony was suspended in the electrolyte by means of a piece of platinum wire.

The vessel for the auxiliary hydrogen electrode consists of the tap funnel already mentioned. It served likewise for introducing hydrogen into the vessel before an experiment. The tap, having been freed from grease, was kept closed during measurements, the electrolyte around the barrel providing the electric connexion. The liquid in the vessel above the tap was, in the case of the experiments with acid electrolytes, always *N*-sulphuric acid; below the tap

FIG. 1.



it was the electrolyte used. In the case of the experiments on alkaline electrolytes, the liquid above the tap was always the same as the electrolyte used. To obtain the theoretical overvoltage, the concentration and temperature of the electrolyte in the hydrogen electrode should be the same as those of the working electrode. A small correction would thus have to be applied to give the theoretical value. This correction would, in the case of the alkaline electrolytes, be negligible; in the case of the acid electrolytes, it would very rarely exceed two centivolts. The numbers given have therefore not been corrected, but are those directly observed. The platinum plates of the hydrogen electrode were platinised in the usual manner. The principal dimensions were approximately 2 and 1.5 cm., and about one-half was immersed in the electrolyte. The hydrogen was obtained from a cylinder of compressed commercial hydrogen. It was washed by means of alkaline permanganate. The porous pot was placed in a beaker containing electrolyte of the same composition as that in the pot, which reached well up to the level of the cork. The whole was immersed in a water-bath in which it could be heated to the desired temperature.

For the purpose of obtaining and regulating the current, a battery was connected with the two end-terminals of a sliding rheostat, and the current required was shunted off from one terminal and the slider. The circuit comprised the electrolytic cell, a calibrated ammeter of the moving-coil type, and the rotary commutator. The latter, as already explained, connected the cathode alternately with the source of current and with the auxiliary hydrogen electrode through a potentiometer. Two rotary commutators were employed in various experiments, and the results obtained by both were the same. The first was a commutator constructed for the determination of electrolytic resistances by Whetham's method, only three of the eight brushes being employed in the present instance. During one revolution, the cathode was four times connected with each of the two circuits. The commutator was driven by a belt, the number of revolutions of which could easily be counted, so that a knowledge of the ratio of revolutions of belt to revolutions of the commutator allowed the latter to be calculated. The other commutator was specially constructed for the present work and therefore could be made of much simpler design. It connected the cathode twice with each of the two circuits per revolution. It was driven directly at a very high speed from the shaft of a small electromotor by means of a flexible connexion consisting of a piece of rubber tube. Attempts to count the speed of this commutator directly by means of a speed-counter failed owing to slowing down of the motor; the fact, however, that this commutator gave the

same results as the other one, running at its highest speed, proved that its speed was at least equal to that of the latter. A complete series of tests was carried out, both in acid and in alkaline solutions at all the concentrations and temperatures investigated, to determine the effect of speed of the commutator on overvoltages, and showed that under all conditions it was possible to obtain values that were independent of further increase of speed. In the more concentrated solutions, it was necessary to employ a slightly higher speed than in the more dilute ones; the temperature, however, had little influence on the minimum speed required. The numbers taken from these experiments which are given in Table I will convey

TABLE I.

Breaks of current per minute	1200	1750	2150	3000	3300	3700
Over- ϵ (N/32-H ₂ SO ₄ at 80°)	0.621	0.632	0.632	0.632	0.632	0.632
voltage (8N-H ₂ SO ₄ at 80°)	0.333	0.352	0.385	0.406	0.407	0.407
Breaks of current per minute	1000	1300	1650	2650	3050	3650
Over- ϵ (N/32-NaOH at 45°)	0.645	0.655	0.655	0.655	0.655	0.655
voltage (8N-NaOH at 45°)	0.420	0.440	0.455	0.470	0.475	0.475

a sufficient idea of the effect of speed of commutator on the accuracy of the results. Several potentiometers were employed in this work. They were either of the Poggendorf or of the voltmeter compensation type (Sand, *Trans. Faraday Soc.*, 1909, 5, 162). They were compared with each other and gave the same results.

Results in Acid Solution (Experiments by S. W. WORRELL).

The experiments were carried out on sulphuric acid solutions made by diluting standard stock solutions. In Table II are given results on the variation of overvoltage with current density. It

TABLE II.

Variation of overvoltage with current density in acid solution.

Strength of acid.	N 32.	2N.	N 4.	N/2.
Temp.	50°.	50°.	20°.	30°.
Millicamps.	Over-	Over-	Over-	Over-
per sq. cm.	voltage.	voltage.	voltage.	voltage.
1	0.080	0.050	0.080	0.050
2	0.239	0.130	0.250	0.133
3	0.370	0.233	0.400	0.250
4	0.510	0.360	0.530	0.400
5	0.606	0.473	0.620	0.530
6	0.660	0.513	0.625	0.600
7	0.680	0.525	0.684	0.640
8	0.688	"	0.695	0.650
9	"	"	"	"
10	"	"	"	"
11	"	"	"	"
15	"	0.525	0.695	0.650
25	"	"	"	"
50	0.688	"	0.695	0.650
100	—	—	—	"

will be seen that in every case the overvoltage rises until a definite value is reached at a current density in the neighbourhood of 8 milliamperes per sq. cm., and then becomes constant. This value, which we may refer to as the critical current density, varies with temperature and concentration. The corresponding point on the curves we shall refer to as the break-point. In Table IIIa are given results which show that below the break-point no stibine whatever is produced. In Table IIIb the yield of stibine is shown

TABLES IIIa and IIIb.

Variation of yield with current density in acid solution.

Temp.	Conc. of acid.	Milliamps. per sq. cm.	Over-voltage.	Critical over-voltage.	Yield per cent.
(a) Current below the critical density.					
20	N	7	0.615	0.620	0
50	"	"	0.560	0.573	"
30	N/2	"	0.640	0.650	"
30	N/8	"	0.690	0.696	"
50	N/32	"	0.675	0.688	"
20	2N	"	0.550	0.570	"
30	"	"	0.550	0.560	"
20	4N	6	0.520	0.532	"
20	8N	"	0.510	0.520	"
50	"	5	0.445	0.453	"
70	N	6	0.520	0.530	"
70	N/2	"	0.560	0.575	"
(b) Current above the critical density.					
20	N	7	0.620	0.620	11.35
"	"	20	"	"	11.51
"	"	50	"	"	11.80
"	"	100	"	"	12.21
"	"	150	"	"	12.22
50	"	8	0.573	0.573	7.95
"	"	20	"	"	8.00
"	"	50	"	"	8.21
"	"	100	"	"	8.46
"	"	150	"	"	8.46
40	N/2	8	0.634	0.634	5.07
"	"	20	"	"	5.14
"	"	50	"	"	5.44
"	"	100	"	"	5.53
"	"	150	"	"	5.55

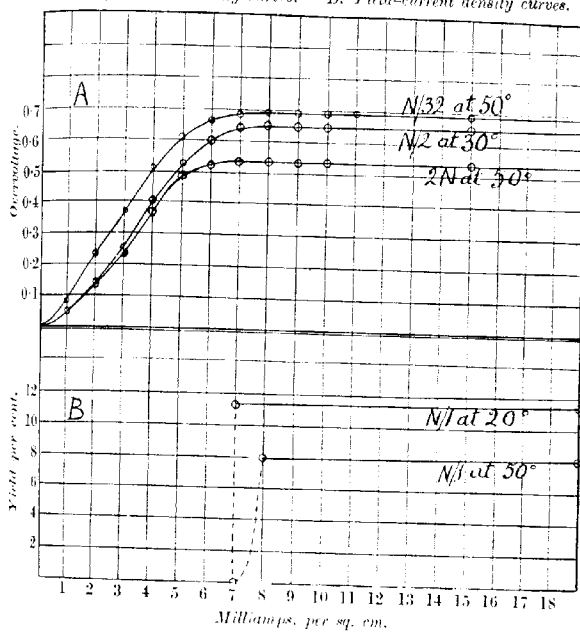
at various current densities above the break-point. It will be seen that the effect of current density on yield at given temperatures and concentrations is slight, the yield increasing to a constant value. It may be noted here that the yield is dependent also on the presence of other metals. Thus, experiments were carried out in which the cathode consisted either of copper or of platinum gauze, plated electrolytically with antimony from a thioantimonite solution. The overvoltage was found the same as with solid antimony. The yield, however, differed. Thus, in one instance,

11.80 per cent. of stibine was obtained from pure antimony, 7.55 per cent. from antimony deposited on platinum gauze, and 7.27 per cent. from antimony deposited on copper gauze. Some of the results of Tables II, IIIa, and IIIb are expressed graphically in Fig. 2 in two sets of curves. In the upper, the abscissæ are current densities, the ordinates overvoltages. In the lower set, the abscissæ are the same as in the upper one, and the ordinates represent yields. The figure thus illustrates the connexion between yield and break-point.

FIG. 2.

Acid solution.

A. Overvoltage-current density curves. B. Yield-current density curves.



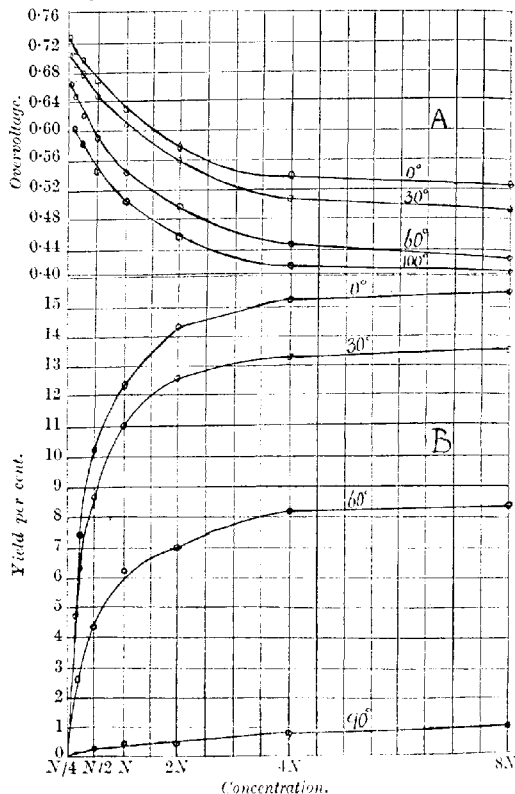
In the following experiments a current of 50 milliamperes was always employed, which is considerably greater than the critical value (about 8 milliamps./cm.²). At this current density, the yield has also nearly reached its maximum value. The results are represented graphically in Figs. 3 and 4, the tables containing the actual numerical values having been omitted to economise space. It will be seen that at a given temperature the overvoltage

starts from a high value at low acid concentration, and with increasing concentration gradually approaches a value which becomes almost independent of further increase of concentration. Similarly, at constant concentration, overvoltage decreases with increasing

FIG. 3.

Acid solution.

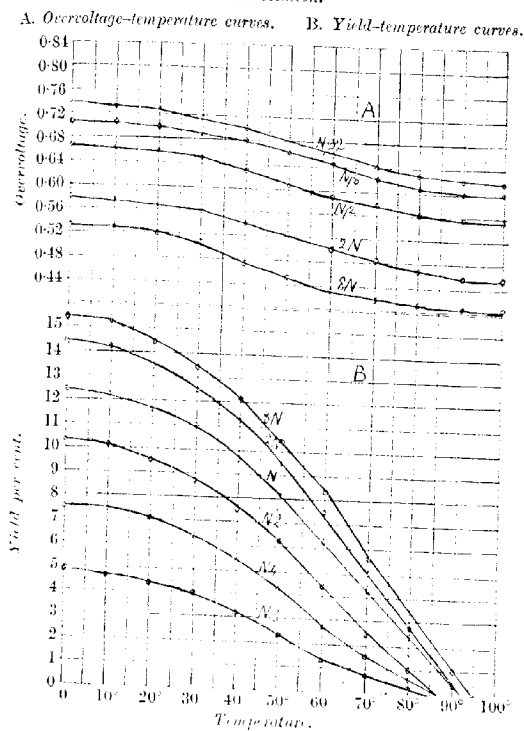
A. Overvoltage-concentration curves. B. Yield-concentration curves.



temperature. The highest value found for overvoltage was 0.740 in an $N/32$ -solution at 0° . In the same solution, the overvoltage was 0.625 at 100° . In an $8N$ -solution, on the other hand, the overvoltage was 0.530 at 0° and 0.400 at 100° . As regards yield,

the following extreme numbers may be quoted. In an $N/32$ -solution 0.65 per cent. was obtained at 0° and only a trace at 40° . In a $4N$ -solution, on the other hand, the yield was 15.23 per cent. at 0° and became practically zero only at 95° . At still higher concentration the total yields were still higher, but as already

FIG. 4.
Acid solution.



explained, a considerable proportion of the stibine originally formed was here decomposed in contact with the electrolyte.

Results in Sodium Hydroxide Solution (Experiments by E. J. WEEKS).

The electrolyte for these experiments was made up from carefully standardised stock solutions as in the case of the acid solutions.

TABLE IV.

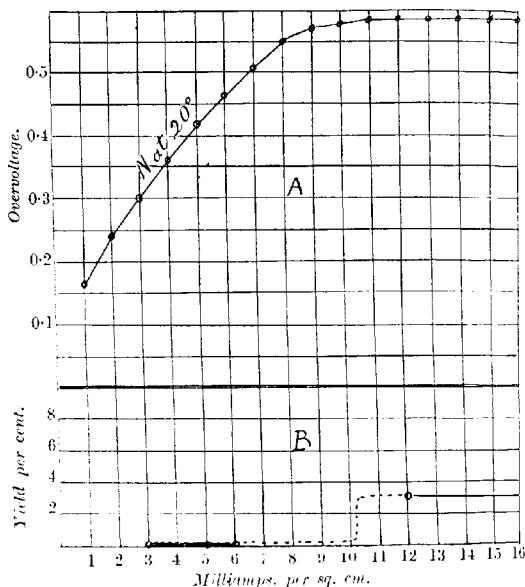
Variation of overvoltage with current density in *N*-NaOH solution at 20°.

Milliamps. per sq. cm.	1	2	3	4	5	6	7	8
Overtoltage	0.17	0.24	0.30	0.36	0.42	0.47	0.51	0.55
Milliamps. per sq. cm.	9	10	11	12	13	14	15	50
Overtoltage	0.57	0.58	0.59	0.59	0.59	0.59	0.59	0.59

FIG. 2A.

Sodium hydroxide solution.

A. Overtoltage-current density curve. B. Yield-current density curve.



In Table IV are given results showing the variation of overvoltage with current density for *N*-sodium hydroxide at 20°. As with the acid solutions, the overvoltage becomes quite constant when the break-point corresponding with about 11 milliamps. per sq. cm. is reached. The results given in Table Va show that below the break-point no stibine at all is produced. In Table Vb are given the total yields of stibine produced at current densities above the critical value, and also the separate portions collected as gas and as metallic antimony. It will be seen that the total yield varies only very

TABLES Va and Vb.

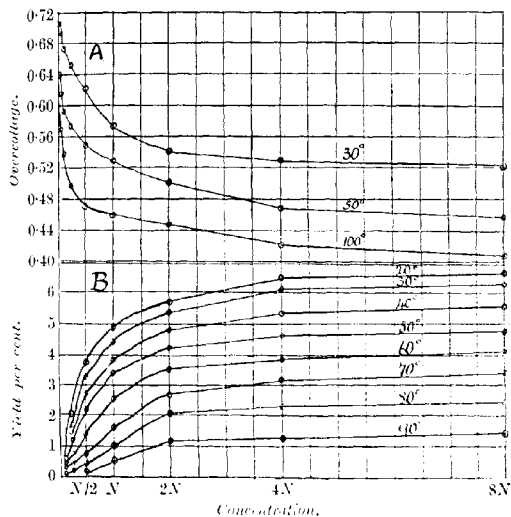
Variation of yield with current density in *N*-NaOH solution at 20°.

Milliamps. per sq. cm.	Overtoltage.	% Yield as gas.	% Yield as metal.	Total % yield.
(a) Current below the critical density.				
3	0.30	0	0	0
5	0.42	"	"	"
6	0.47	"	"	"
(b) Current above the critical density.				
12	0.59	0.448	4.35	4.98
52	"	0.472	4.39	4.862
80	"	0.473	4.41	4.883
150	"	"	"	"

FIG. 3A.

Sodium hydroxide solution.

A. Overtoltage-concentration curves. B. Yield-concentration curves.



slightly with increase of current density, becoming constant above about 50 to 80 milliamps. per sq. cm. Fig. 2a represents the results of Tables IV, Va, and Vb graphically.

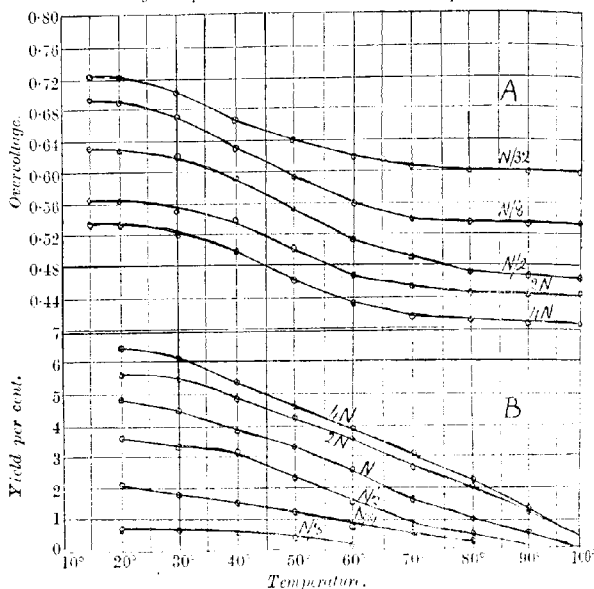
In the following experiments the variation of overvoltage and of yield with concentration and temperature of the caustic soda was examined. The current density employed was uniformly

50 milliamperes per square centimetre, a value well above the critical current density of about 11 milliamperes per square centimetre. The results are plotted in Figs. 3a and 4a. The same general remarks hold that were made with regard to the experiments in acid solution. It will be noted, however, that the total yield is very much smaller and of this, less than one-tenth left the solution as stibine gas.

FIG. 4A.

Sodium hydroxide solution.

A. Overvoltage-temperature curves. B. Yield-temperature curves.



Summary, and Discussion of Results.

(1) The fact has already been referred to, that for an electrolyte of given composition and temperature the overvoltage becomes practically independent of current density after a certain "critical" value has been reached. Below this value no stibine whatever is produced, above it a yield is obtained that is influenced only very slightly by further increase of current density.

(2) Perhaps the most surprising result obtained is the very great analogy between the curves for acid and for alkaline solution.

At low concentration we have in both cases very high overvoltages but practically no yield of stibine; with increasing concentration of the acid or alkali, the overvoltage, however, diminishes to a value almost constant at each temperature, while the yield slowly increases. We may conclude from these results that both acid and alkali act as catalysts, promoting the union between the antimony of the cathode and the hydrogen which is being produced with a large amount of free energy. Such catalysts we should expect to cause the decomposition of the stibine formed, when it has passed from the electrode into the liquid, where it is unstable. In agreement with this, we find that some of the stibine is decomposed in the most concentrated acid solutions, and in all the alkaline ones. With rise of temperature the overvoltage decreases, the yield of stibine becoming smaller and finally zero. It is probable that these two facts are closely connected, the free energy of the nascent hydrogen gradually becoming too small with rise of temperature to allow it to form stibine.

(3) From the results given, it is apparent that the electrolytic process for the preparation of stibine is quite capable of competing with other methods, the most favourable conditions being represented by a compact antimony electrode in an acid solution of about 4*N*-strength, employed at a low temperature and with a current density greater than the critical value of 10 milliamperes per sq. cm. A yield of about 15 per cent. by volume may be thus obtained.

(4) *Free Energy of the Reaction* $2\text{Sb} + 3\text{H}_2 = 2\text{SbH}_3$.—If the combination between antimony and hydrogen took place reversibly at the cathode, the overvoltage would allow us to calculate the free energy of the reaction, since this would be equal to the free energy of the nascent hydrogen (referred to ordinary molecular hydrogen). If f is the free energy of two mols. of stibine of temperature T and atmospheric pressure, and π the overvoltage of the hydrogen producing this substance, then the relation would hold:

$$f = 6 \times 96540\pi.$$

This value, it appears, must be considered an upper limit on almost any theory of overvoltage. Owing to the very considerable catalytic activity of the acid and the alkali in the more concentrated solutions, particularly at a high temperature, it may be taken that the correct value of the free energy of the reaction will not be very far removed from that calculated by the above formula. Thus at 90° an overvoltage of 0.402 was observed in acid solution, stibine of a partial pressure of 0.01 atmosphere being produced. This corresponds with a free energy value of $6 \times 96540 \times 0.402 \times$

$2.389 \times 10^{-4} = 55.6$ large calories per two mols. To obtain the corresponding value for atmospheric pressure, we must add to the foregoing $2RT \log_e 1/0.01$, that is, 6.46 large calories, making 62.1 large calories per 2 mols. of stibine at atmospheric pressure. ($R = 1.987 \times 10^{-3}$ large calories per mol. and degree; $T = 363^\circ$). In alkaline solution, we have an overvoltage of 0.404, producing in the first instance stibine of 0.0131 atmosphere pressure, and this yields for atmospheric pressure the almost identical value of 62.0 large calories per two mols. of stibine.

In a similar manner, we find from the experiments on acid solution at 20° , making $T = 293^\circ$ and $\pi = 0.520$ volt, that the free energy of two mols. of stibine of 0.1452 atmosphere partial pressure is 72.0 large calories, which gives a value for stibine under atmospheric pressure of 74.2 calories. The experiments on alkaline solutions, according to which the overvoltage at 20° is 0.533 for the production of stibine of 0.0623 atmosphere partial pressure, yield for the free energy of two mols. of stibine at atmospheric pressure the value 77.0 calories.

According to Stock and Wrede (*Ber.*, 1908, **41**, 540), the heat of formation of stibine is -34.27 large calories per mol., a value about two and a half times as large having been previously determined by Berthelot and Petit (*Compt. rend.*, 1889, **109**, 546). Taking Stock and Wrede's figure, the internal energy of two mols. of stibine is 68.5 calories, which is very close to the values for free energy suggested above. If we indicate the internal energy of the system by U and make $f = -A$, then according to the Gibbs-Helmholtz equation the gradient of free energy with temperature is given as

$$df/dT = -dA/dT = (f - U)/T.$$

Substituting the values given above for f and for U , we find that at 100° df/dT is approximately zero, which agrees with the overvoltage-temperature curves. The values suggested for f at the ordinary temperature would lead to a very small positive temperature gradient for free energy, in contrast to the negative one following from the curves. It is therefore probable that these free-energy values are slightly high.

Experiments are being continued on the relation between yield of stibine and overvoltage, and the concentration of hydrogen- and hydroxyl-ions in the electrolyte; and also on the conditions governing the nature of the deposit from solutions containing metal-ions.

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[Received, November 24th, 1922.]

LIX.—*The System Chromium Trioxide-Nitric Acid-Water.*

By STANLEY AUGUSTUS MUMFORD and LIONEL FELIX GILBERT.

THE solubility of chromium trioxide in nitric acid does not appear to have been systematically investigated. The purification of the anhydride by washing with nitric acid was advocated by Bunsen (*Annalen*, 1868, 148, 290) and later by Zettnow (*Pogg. Ann.*, 1871, 143, 468), the former employing "fuming nitric acid containing no nitrous oxides," the latter "nitric acid of not less than 1.46 sp. gr.," in which acid chromium trioxide is stated to be insoluble; but no later data can be traced.

TABLE I.

Compositions (grams per 100 grams) and densities at 25°.

d_4^{25}	Liquid phase.		Wet solid.	
	HNO ₃ .	CrO ₃ .	HNO ₃ .	CrO ₃ .
1.704	0	62.85	—	—
1.684	2.28	60.31	—	—
1.661	5.95	56.47	2.47	78.76
1.640	9.37	52.51	—	—
1.606	13.25	48.10	6.96	74.87
1.570	19.30	41.97	8.62	74.90
1.528	26.79	34.32	12.10	70.43
1.481	35.35	25.54	—	—
1.434	46.91	14.63	19.73	62.96
1.402	59.11	4.88	23.24	61.45
1.409	68.49	0.95	46.97	32.05
1.440	74.47	0.27	36.09	50.90
1.456	82.90	0.06	44.18	46.19
1.466	86.56	0.10	—	—
1.475	89.17	0.18	51.38	41.52
1.503	92.63	1.89	40.54	56.11
1.557	91.36	8.29	44.64	55.03

TABLE II.

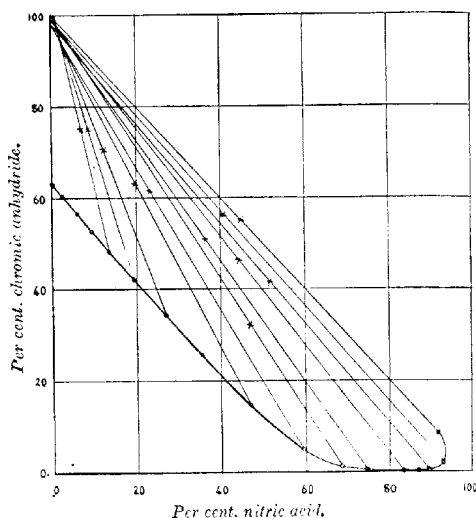
Compositions (grams per 100 grams) and densities at 45°.

d_4^{45}	Liquid phase.		Wet solid.	
	HNO ₃ .	CrO ₃ .	HNO ₃ .	CrO ₃ .
1.695	0	63.51	—	—
1.676	2.05	61.27	—	—
1.654	5.58	57.93	4.13	75.48
1.619	11.47	51.71	—	—
1.589	19.53	45.41	10.18	68.32
1.490	33.29	29.57	—	—
1.409	50.60	13.15	39.77	31.99
1.384	65.74	2.47	27.60	59.82
1.416	73.81	0.88	30.33	57.57
1.450	81.55	0.44	41.50	46.93
1.481	88.35	0.60	61.21	29.62
1.512	91.83	3.39	—	—
1.581	88.06	9.42	65.82	30.55

In the present paper the results of a determination of the solubility isotherms of the system $\text{CrO}_3\text{-HNO}_3\text{-H}_2\text{O}$ at 25° and 45° are described.

The system is of a comparatively simple character, the composition of the solid phase, as determined by the "wet solid" method, being CrO_3 throughout. The two isotherms are precisely similar in type; they exhibit no discontinuity, and differ only in the slightly greater solubilities of the anhydride at the higher temperature.

In the tables of results (Tables I and II) the compositions of the



liquids and wet solids are expressed in grams per 100 grams, and the densities of the liquids are those in a vacuum. The values obtained at 25° have been plotted in the diagram.

It will be observed that the minimum solubility of chromium trioxide occurs in approximately 18*N*-nitric acid (80 per cent.), corresponding with the acid of d^{15} 1.46 mentioned by Zettnow. It is of interest that an acid of this strength corresponds with the molecular ratio $\text{HNO}_3\text{,H}_2\text{O}$; and further, that the subsequent increase in solubility of the anhydride does not take effect until after the ratio $2\text{HNO}_3\text{,H}_2\text{O}$ has been passed. It would therefore appear that hydration of the nitric acid may play an important part in determining the solubility relations in the system.

The colours of the solutions change with increasing concentration of nitric acid from dark red to yellow, the solutions on the flat portion of the curve being light yellow. The solutions in the strongest nitric acids (95 and 99 per cent. with the 25° isotherm, 95 and 97 per cent. with the 45° isotherm), however, are again dark red, and this, taken in conjunction with the increased solubility of chromium trioxide, appears to point to polymerisation or to formation of compounds.

The densities of the systems may be calculated with a considerable degree of accuracy by employing the equation involving assumption of the constancy of the molecular volumes of the components in the solutions (Masson, T., 1911, 99, 1132), namely,

$$\alpha a + \beta b + \gamma w = 1000,$$

where a , b , and w are the concentrations in gram-molecules per litre of the nitric acid, chromium trioxide, and water, respectively, and α , β , and γ the corresponding molecular solution volumes. Transformed for the calculation of densities, the equation becomes

$$D = K + k_1 a + k_2 b,$$

where D is the density of the solution containing a gram-molecules of nitric acid and b gram-molecules of chromium trioxide per litre, and the constants K , k_1 , k_2 are directly calculable from the values of α , β , and γ . For the 25°-series, the equation is

$$D = 1.1476 + 0.01663 a + 0.05198 b,$$

and the calculated densities are in excellent agreement with the observed values, the calculated densities corresponding with the first eleven measured (corrected) densities given in Table I being as follows: 1.704, 1.685, 1.661, 1.636, 1.605, 1.570, 1.528, 1.482, 1.434, 1.402, 1.409. At neither temperature, however, does the assumption of constant molecular solution volume hold for concentrations of nitric acid higher than 17N.

Subsequent to the publication of the paper referred to above, Dr. Masson has shown (private communication) that the concordance of the values calculated by the above equations with fact is probably due, not to constancy of molecular volumes, but to counterbalancing variations in these. The equations are therefore empirical but useful. This matter was studied in the present case, for which purpose the densities of unsaturated aqueous solutions of chromium trioxide were determined (Table III). The specific volumes of nitric-chromic solutions in water prove to be only approximately additive functions of those of the two solutions taken separately.

TABLE III.

Densities of aqueous chromic acid solutions (M = gram-molecules per litre).

At 25°.		At 45°.	
d_4^{25}	M.	d_4^{45}	M.
1.7042	10.713	1.6954	10.768
1.5707	8.627	1.6060	9.331
1.4835	7.288	1.5277	8.173
1.4135	6.221	1.4593	7.034
1.3479	5.171	1.3813	5.896
1.2901	4.301	1.3056	4.733
1.2491	3.536	1.2379	3.663
1.1967	2.886	1.1831	2.829
1.1530	2.222	1.1306	2.069
1.1134	1.649	1.0918	1.467
1.0815	1.193	1.0599	1.002
1.0602	0.842	1.0226	0.459
1.0256	0.398	1.0063	0.226
1.0119	0.206		
1.0042	0.098		
1.0012	0.060		
0.9989	0.029		
0.9981	0.013		

It is of interest to note that the densities of the ternary solutions are within 0.25 per cent. of those calculated from the law of mixtures on the hypothesis that each solution consists of a saturated solution of chromium trioxide in water, mixed with a solution of nitric acid in the remaining water, and when the latter solution contains nitric acid and water in the molecular ratio 1.2 the ternary mixture is found to have the minimum density.

EXPERIMENTAL.

Components.—The chromium trioxide and nitric acid (up to 69 per cent.) used were of the standard of purity demanded by the "A. R." tests. The strongest nitric acid was obtained by distillation in an all-glass apparatus, with the exclusion of light, of a mixture of the 69 per cent. acid with two volumes of pure concentrated sulphuric acid, and subsequent fractional redistillation under reduced pressure (75–90 mm.) from a small quantity of pure dry barium and silver nitrates (compare Velej and Manley, *Phil. Trans.*, 1898, 191, [4], 365). The first fractions of the second distillation were bright orange-yellow and contained about 1.5 per cent. of nitrous acid, which, however, was not removable by the passage either of carbon dioxide through the warm acid (compare Millon, *J. pr. Chem.*, 1843, 29, 349), or of ozone in the cold. The later fractions contained about 99 per cent. HNO_3 , and were either colourless or very slightly pale yellow, only traces of nitrous acid

being present. Nitrous-free acid only was employed in the concentrated acid systems at 25°, the acid used for those at 45° being slightly yellow in colour and containing up to 0.4 per cent. of nitrous acid.

Procedure.—The components were mixed in suitable proportions, the less concentrated systems being sealed in glass tubes of about 100 c.c. capacity and revolved in a thermostat, the more concentrated systems being contained in small glass-stoppered bottles and suspended with repeated shaking in the thermostat. Sampling was effected in the same way as described in a recent paper by Gilbert, Buckley, and Masson (T., 1922, 121, 1934), the operations being performed as rapidly as possible to minimise absorption of atmospheric moisture and loss of nitric fumes.

Analytical Methods.—The total acidity of the samples was determined by titrating the suitably diluted mixture with *N*/10-barium hydroxide, using phenolphthalein, the colour change of which is not interfered with by the pale yellow precipitate of barium chromate. The method was shown by means of careful tests to yield results accurate to within 0.1 per cent. Estimation of the chromic acid by the iodometric process being here inapplicable owing to the presence of nitric acid (plus traces of nitrous acid), the chromate, in all but the solutions containing little chromium trioxide, was estimated gravimetrically by precipitation as mercurous chromate and ignition of the precipitate. In the latter solutions the chromate was estimated by addition of an excess of *N*/10-ferrous ammonium sulphate and subsequent titration with *N*/10-permanganate to determine the excess. Both methods were tested over the range of concentrations employed and shown to be accurate to within 0.15 per cent. Nitric acid was estimated by difference, the tests showing that in all but the very dilute nitric acid systems no error greater than 0.2 per cent. was obtained.

This work was carried out at the suggestion of Dr. Irvine Masson, to whom our thanks are due for much helpful advice. One of the authors (S.A.M.) wishes to express his indebtedness to the Department of Scientific and Industrial Research for a grant.

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(Received, January 12th, 1923.)

LX.—*The Action of Alcohol on the Sulphates of Ammonium.*

By HORACE BARRATT DUNNICLIFF.

WHEN dry sodium hydrogen sulphate is treated with dry alcohol, it yields $\text{Na}_2\text{H}(\text{SO}_4)_2$, but a similar reaction is not observed when dry potassium hydrogen sulphate is treated with dry alcohol (Butler and Dunnicliff, T., 1920, 117, 649). The object of the work to be described was to investigate the action of alcohol on ammonium sulphate and ammonium hydrogen sulphate and to determine the best method for the preparation of the compound $(\text{NH}_4)_2\text{H}(\text{SO}_4)_2$ originally reported by Mitscherlich (*Pogg. Ann.*, 1836, 39, 198) and later by van Dorp (*Z. physikal. Chem.*, 1910, 73, 284) and D'Ans (*Z. anorg. Chem.*, 1913, 80, 235).

Preparation of Materials.—Alcohol was dried with lime as described in the previous work (*loc. cit.*), and controls were carried out on sodium and potassium hydrogen sulphates. The alcohol was considered ready for use if sodium hydrogen sulphate, when treated with five times its weight of alcohol, gave a product having an acidity of not less than 18.60 per cent. or if potassium hydrogen sulphate, similarly extracted, gave a product showing a fall of acidity of not more than 0.3 per cent. All the early experiments were carried out with lime-dried alcohol, but subsequently considerable quantities of alcohol were dried by the following method.

Alcohol (absolute) was treated with small pieces of calcium carbide. Effervescence took place and continued for some time. The alcohol was then boiled on a water-bath for some hours over fresh calcium carbide under reflux. After cooling, the total cessation of evolution of gas was observed by connecting an alcohol manometer to the flask. The spirit was first distilled under reduced pressure, and the runnings, which at first had an unpleasant odour, were discarded until practically no foreign smell was noticeable in the distillate. The main bulk of the alcohol was then distilled from a water-bath at atmospheric pressure. B. p. 77.1–77.2°/726 mm. (Lahore).

The alcohol had a slight foreign odour, but no impurity could be detected. The efficiency of this alcohol as tested by controls showed that it is indistinguishable for the present purpose from the best samples of alcohol dried by the lime method.

Ethyl ether, alcoholic sulphuric acids, sodium sulphate, and sodium hydrogen sulphate were prepared by the methods already described (*loc. cit.*).

Ammonium Sulphate.—Ammonia gas from pure ammonia

"fortis" was passed into a solution of pure sulphuric acid in water until the solution smelt of ammonia and the reaction was alkaline. The crystals were filtered off and left on a porous plate in a desiccator for fourteen days. The ammonium sulphate was powdered and extracted with dry ether in a Soxhlet apparatus (Found: $\text{SO}_4 = 72.76$; $\text{NH}_4 = 27.39$. Calc. for $(\text{NH}_4)_2\text{SO}_4$, $\text{SO}_4 = 72.70$; $\text{NH}_4 = 27.30$ per cent.).

Ammonium Hydrogen Sulphate.—Molecular proportions of sulphuric acid and ammonium sulphate were dissolved in water and concentrated on a water-bath until crystals separated. The solution was cooled and the crystals which separated were quickly pressed between filter paper and then left on a porous saucer in a desiccator over sulphuric acid for some days. The crystals were extracted with ether in a Soxhlet apparatus until the runnings were neutral. This was found to be the most efficient method for the elimination of traces of water and sulphuric acid from the product (Found: $\text{H}_2\text{SO}_4 = 42.56$; $\text{SO}_4 = 83.45$; $\text{NH}_4 = 15.59$. Calc. for NH_4HSO_4 , $\text{H}_2\text{SO}_4 = 42.61$; $\text{SO}_4 = 83.47$; $\text{NH}_4 = 15.67$ per cent.). M. p. 145.0° . The substance is extremely hygroscopic and was preserved in glass bottles in desiccators.

Action of Alcohol or Ether on Ammonium Sulphate.—Ammonium sulphate is not attacked by either dry alcohol or dry ether. If the sample contains any moisture, either of these two solvents extracts it.

Action of Alcohol or Ether on Ammonium Hydrogen Sulphate.—Ether has no action on ammonium hydrogen sulphate except to extract traces of moisture or free sulphuric acid from it.

Ammonium hydrogen sulphate ($\text{H}_2\text{SO}_4 = 42.56$ per cent.) was shaken with seven times its weight of dry alcohol for eighteen hours. The product was quickly filtered and then extracted with ether in a Soxhlet apparatus. The washing was complete when litmus paper from which the ether had completely evaporated was unchanged by the extract. A typical sample of the product gave the following analysis: $\text{H}_2\text{SO}_4 = 19.73$; $\text{SO}_4 = 77.77$; $\text{NH}_4 = 21.72$. Theory for $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$ requires $\text{H}_2\text{SO}_4 = 19.84$; $\text{SO}_4 = 77.69$; $\text{NH}_4 = 21.90$ per cent. Hence the action of seven parts of alcohol on one part of ammonium hydrogen sulphate is to give an intermediate sulphate having the formula $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$, corresponding with that formed by the action of alcohol (7 parts) on sodium hydrogen sulphate (1 part). The alcohol first rapidly extracts the sulphuric acid and partial esterification follows. Similar results are obtained when the ratio of alcohol to NH_4HSO_4 is 5:1. This triammonium hydrogen disulphate is not deliquescent and decomposes before melting. On treatment with a fresh quantity

of dry alcohol, $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$ loses a further small quantity of acid (0.3 to 0.5 per cent.) (compare T., 1920, 117, 653). This reduction of acidity is not observed when the compound is treated with alcoholic sulphuric acid (about 3.8 per cent. H_2SO_4) produced in a previous extraction.

Commercial "Pure" Ammonium Hydrogen Sulphate.—By taking advantage of this reaction, the constitution of commercial samples of ammonium hydrogen sulphate may be investigated by a similar procedure to that given in T., 1920, 117, 666 for the determination of the constitution of nitre cake.

All the samples of commercial "pure" ammonium hydrogen sulphate available contained moisture. They were dried by ether extraction. No dried sample examined had a higher acidity than 38.00 per cent. In examining the constitution on the analogy of nitre cake (*loc. cit.*), three possibilities have to be considered.

- (a) The commercial hydrogen sulphate is a mixture of ammonium sulphate and ammonium hydrogen sulphate,
- (b) it is a mixture of ammonium sulphate, ammonium hydrogen sulphate, and intermediate sulphate, or
- (c) it is a mixture of ammonium hydrogen sulphate and the intermediate sulphate.

It is possible to distinguish between these three: (a) and (b) will be acted upon by alcohol, giving a product which has an acidity lower than that of the intermediate sulphate (19.84 per cent.), since, in each case, the ammonium hydrogen sulphate will be acted upon by the alcohol, giving $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$, and the normal sulphate will act as a diluent and diminish the acidity of the product.

To distinguish between (a) and (b), use is made of the fact that, in the former case, alcohol extracts two-thirds of the total acid present, whilst, in the latter case, less than two-thirds of the acid present is extracted by treatment with alcohol.

In the third case, (c), the acidity of the product after treatment of the commercial hydrogen sulphate with alcohol will be 19.84 per cent. or thereabouts.

Analysis of a particular sample of dried "pure" ammonium hydrogen sulphate before treatment with alcohol gave $\text{H}_2\text{SO}_4 = 37.66$; $(\text{NH}_4)_2\text{SO}_4 = 62.41$. Theory for NH_4HSO_4 requires $\text{H}_2\text{SO}_4 = 42.61$; $(\text{NH}_4)_2\text{SO}_4 = 57.39$ per cent.

After extraction with alcohol (5 parts) and washing with ether, analysis gave: $\text{H}_2\text{SO}_4 = 19.66$; $\text{NH}_4 = 21.81$; $\text{SO}_4 = 77.74$. Theory for $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$ requires $\text{H}_2\text{SO}_4 = 19.84$; $\text{NH}_4 = 21.90$; $\text{SO}_4 = 77.69$ per cent.

Hence the dried commercial hydrogen sulphate examined consists

of a mixture of ammonium hydrogen sulphate (78.25 per cent.) with the intermediate sulphate (21.75 per cent.).

Calculation shows that, had the sample consisted of a mixture of ammonium sulphate with the hydrogen sulphate, the theoretical acidity after alcohol treatment and washing with ether would have been 16.76 per cent.

Preparation of the Intermediate Sulphate.—This was attempted by the following methods :

(1) When ammonium sulphate is mixed with ammonium hydrogen sulphate and the mixture raised to a temperature of 190° , the intermediate sulphate is formed as in the case of the sodium salts (*loc. cit.*). With excess of the hydrogen sulphate, a quantitative result is obtained, but the explanation of the preparation is complicated by the fact that ammonium sulphate readily decomposes when heated and will itself give the intermediate sulphate (when heated in a platinum dish to 320°) (W. Smith, *J. Soc. Chem. Ind.*, 1895, 14, 629; 1896, 15, 3). The products of the action of ammonium sulphate with excess of fused ammonium hydrogen sulphate gave, on treatment with alcohol, residues having acidities ranging from 19.66 to 19.82 per cent.

(2) Action of concentrated sulphuric acid on dry ammonium sulphate. The two substances were triturated together and then put into a desiccator. Original acidity of the product = 20.34 per cent. Acidity after extraction with ether = 15.26 per cent. This indicates that about 25 per cent. of the acid had, up to that time, failed to combine with the ammonium sulphate to form either of the compounds under investigation. After twenty-four hours, the ether-extracted substance had an acidity of 16.23 per cent. Determinations of acidity after treatment with alcohol for twenty-four hours and subsequent extraction with ether gave the following results :

(a) Immediately after trituration	5.89 per cent.
(b) About four hours after trituration	7.46 " "
(c) Thirty-six hours after trituration	10.30 " "

Theoretical acidity, if all the acid were combined as ammonium hydrogen sulphate, = 7.80 per cent.

These results indicate that the system $(\text{NH}_4)_2\text{SO}_4\text{--H}_2\text{SO}_4\text{--H}_2\text{O}$ is gradually coming to a state of equilibrium. The first combination is probably as hydrogen sulphate, and although the intermediate sulphate is subsequently formed (c), a quantitative result has never been obtained. The possibility that the intermediate sulphate is formed to this extent by the action of alcoholic sulphuric acid (produced by the action of alcohol on the hydrogen sulphate present)

on the ammonium sulphate is negated by a subsequent series of experiments (*vide infra*).

(3) When a solution of ammonium sulphate (3 mols.) and sulphuric acid (1 mol.) was evaporated on a water-bath until the residue appeared to be dry, analysis showed the presence of a notable quantity of water. After being left in an air-oven at 110–120° for seven to eight hours, the acidity of the substance was always high, that is, the percentage of acid was greater than corresponded with the weight of acid added (19.84 per cent.). Seven separate preparations yielded acidities varying between 20.95 and 22.45 per cent. and, after extraction with ether, the acidities rose to 20.99–22.50 per cent. These results were only consistent in the high percentage of acid and suggested that the substance was decomposing with evolution of ammonia. Dry triammonium hydrogen disulphate, prepared by the action of alcohol on ammonium hydrogen sulphate, was left in the oven at about 120° for several hours, and the acidity rose from 19.75 to 20.08 per cent. This method was therefore also rejected.

(4) Instead of attempting to drive off by heat the last traces of moisture from the preparation made according to method (3), drying by ether extraction was tried. By this means preparations (theoretical acidity 19.84 per cent.) having acidities of 19.66–19.43 per cent. were obtained. The acidity of the first ether washings showed that a little acid was still uncombined. If these preparations consist of the intermediate sulphate, treatment with alcohol will only reduce the acidity slightly (not more than 0.5 per cent., p. 478). On treatment of these preparations with alcohol (5 parts) and extraction with ether, residues having acidities ranging from 18.20 to 18.08 per cent. were obtained. If the residue had consisted of a mixture of normal and hydrogen sulphates, the acidities of the residues after alcohol treatment would have been 7.62–7.45 per cent. Hence there is considerable formation of the intermediate sulphate on evaporation and the preparation consists principally of the intermediate sulphate with smaller quantities of the normal and hydrogen sulphates. The possibility that the intermediate sulphate is formed by the action of alcohol on a mixture of ammonium sulphate with the hydrogen sulphate produced by the action of alcoholic sulphuric acids formed in the reaction is denied by direct proof (*vide infra*). The action of alcohol on a mixture of pure ammonium sulphate and pure ammonium hydrogen sulphate sometimes gives an acidity slightly higher than that corresponding to the complete conversion of the hydrogen sulphate into the intermediate sulphate.

(5) Fractional crystallisation. When a solution of equimolecular

quantities of sulphuric acid and sodium sulphate is evaporated and the solid phase which separates is removed at frequent intervals, the latter is found to consist initially of sodium sulphate and later of crystals of increasing acidity. Dried, clear crystals of one crop, A ($\text{H}_2\text{SO}_4 = 18.71$; $\text{Na}_2\text{SO}_4 = 81.16$ per cent.), were treated with seven times their weight of dry alcohol for eighteen hours. The crystals retained their shape and appeared clear and unchanged. After washing with ether, the acidity of the alcohol-treated crystals was 18.49 per cent. The next crop of crystals, B ($\text{H}_2\text{SO}_4 = 20.18$; $\text{Na}_2\text{SO}_4 = 79.70$ per cent.), when similarly treated, gave an acidity of 18.50 per cent. and showed two distinct phases, (1) apparently unchanged crystals, and (2) a white, opaque solid clinging to them. The first crop of crystals, A, appears to be the crystalline modification of the amorphous $\text{Na}_3\text{H}(\text{SO}_4)_2$ produced by the action of alcohol on sodium hydrogen sulphate, and the second crop, B, to consist mainly of A together with some sodium hydrogen sulphate, which has separated as a subsequent phase [$\text{Na}_3\text{H}(\text{SO}_4)_2$ requires $\text{H}_2\text{SO}_4 = 18.71$; $\text{Na}_2\text{SO}_4 = 81.29$ per cent.].

Attempts to prepare triammonium hydrogen disulphate by removing the solid phase at frequent intervals from an evaporating solution of equimolecular quantities of sulphuric acid and ammonium sulphate were unsuccessful. Crops showing promising acidities of about 19.84 per cent. H_2SO_4 proved to be mixtures. Analysis by the method described above under "Commercial 'pure' ammonium hydrogen sulphate" indicated the presence of a large proportion of the intermediate sulphate, but the yield was never even approximately quantitative.

Hence the best method for the preparation of triammonium hydrogen disulphate is by the action of 5 to 7 parts of dry alcohol on 1 part of dry ammonium hydrogen sulphate and extraction of the product of the reaction with ether until the runnings are neutral.

Action of Alcoholic Sulphuric Acids on Ammonium Sulphate and Ammonium Hydrogen Sulphate.

In the analysis of mixtures of the sulphates, the possibility of the vitiation of results recorded above (owing to the action on ammonium sulphate of alcoholic sulphuric acids produced by the action of alcohol on the hydrogen sulphate present) is one that requires attention. Hence the action of alcoholic sulphuric acids of different concentrations on dry ammonium sulphate and ammonium hydrogen sulphate has been examined. As, in the work recorded, the time of reaction had in each case been limited to eighteen hours with shaking, the alcoholic sulphuric acids were allowed to react for that period. For the same reason, the weight

of alcoholic sulphuric acid was always five times the weight of solid taken. These results are therefore not absolute. They were obtained to establish a control and are adequate for the present purpose. The work was done at laboratory temperature. The products of the reaction were extracted with dry ether until the washings were neutral.

TABLE I.

Action of Alcoholic Sulphuric Acids on Ammonium Sulphate.

Percentage of "total" * sulphuric acid.	Hours of ether extraction until washings were neutral.	Percentage acidity of residue after washing with ether.	Percentage acidity of residue after treatment with alcohol and washing with ether.
1.03	2.0	2.01	—
1.71	2.5	3.50	—
2.90	3.0	4.62	—
4.66	4.5	6.50	—
5.90	7.0	8.40	—
7.80	10.0	9.75	—
10.66	18.0	10.45	9.25
21.00	22.0	17.42	15.02
31.00	28.0	19.78	19.04
41.05	37.0	36.93	19.48
51.01	40.0	42.45	19.56
60.68	44.0	42.50	19.62
70.80	50.0	42.62	19.69
80.99	53.0	42.48	19.63

* T., 1921, 119, 1384.

A comparison of the results in column 3 with those for the sodium salt (T., 1920, 117, 658; Table V, column 6) reveals the fact that ammonium sulphate is more readily attacked by the alcoholic sulphuric acids than the sodium salt is by alcoholic sulphuric acids of the same strength. The alcoholic sulphuric acid does not approach exhaustion—an equilibrium is being gradually established between the liquid phase and the solid phases, $(\text{NH}_4)_2\text{SO}_4$ and $x(\text{NH}_4)_2\text{SO}_4 \cdot y\text{H}_2\text{SO}_4$. In these control experiments it is doubtful if the reaction was complete at the lower concentrations.

With ammonium hydrogen sulphate, the equilibrium between the liquid phase and the solid phases appeared to be established. The results suggest changes of solid phase at about 7 * per cent. concentration and somewhere between 21 and 31 per cent. concentration, respectively. The investigation of this ternary system, $(\text{NH}_4)_2\text{SO}_4\text{--H}_2\text{SO}_4\text{--C}_2\text{H}_5\cdot\text{OH}$, is being continued. In a mixture of equimolecular weights of ammonium sulphate and ammonium

* This includes acid originally present in the alcoholic sulphuric acid plus acid extracted from the ammonium hydrogen sulphate.

TABLE II.

Action of Alcoholic Sulphuric Acids on Ammonium Hydrogen Sulphate.

	Percentage of sulphuric acid ("total"),	Hours of ether extraction before washings were neutral.	Percentage acidity of residue after washing with ether.
(i)	1.03	3.0	19.82
(ii)	1.71	3.0	19.86
	2.90	3.5	19.95
	4.66	4.5	20.26
	5.90	6.0	21.76
	7.81	8.0	22.06
	21.00	13.0	28.52
	31.00	16.0	42.64
	41.05	19.0	42.62
	51.00	23.0	42.68

hydrogen sulphate, the acidity extracted from the hydrogen sulphate would make, with the alcohol present, an alcoholic sulphuric acid of about 2.6 per cent. strength. This would have an appreciable action on the ammonium sulphate present and account for the slightly high results obtained for residues after extraction of the mixture with alcohol, and indicating a somewhat high content of $(\text{NH}_4)_2\text{H}(\text{SO}_4)_2$. At the same time, it is possible to distinguish between a mixture of the normal sulphate with (a) the hydrogen sulphate and (b) the intermediate sulphate. In doubtful cases, experiments were repeated in which the weight of alcohol was increased to ten times the weight of solid used in the experiment. In Table II, the total acidity of the liquid phase after extraction in (i) is more than 6 per cent. and in (ii) nearly 7 per cent. The inference is that, in order to obtain triammonium hydrogen disulphate the quantity of alcohol used in the extraction of ammonium hydrogen sulphate should be such that the concentration of the alcoholic sulphuric acid produced is lower than about 6 per cent.

Summary.

(1) Triammonium hydrogen disulphate, $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$, may be prepared by the action of dry alcohol (5–7 parts) on dry ammonium hydrogen sulphate (1 part) and subsequent washing with ether.

(2) Triammonium hydrogen disulphate is not deliquescent. It decomposes before melting and is slightly attacked by pure, dry alcohol.

(3) Commercial ammonium hydrogen sulphates are mixtures of NH_4HSO_4 with $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$ and a little moisture.

(4) Alcoholic sulphuric acids react with the normal and hydrogen sulphates of ammonium more rapidly than alcoholic sulphuric

acids of the same strength do with the normal and hydrogen sulphates of sodium.

I am indebted to Bhai Sachdev Singh for assistance in the experimental work recorded in this paper.

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[Received, October 26th, 1922.]

LXI.—*The Nitration of Benzaldehyde and the Monotropy of o-Nitrobenzaldehyde.*

By OSCAR LISLE BRADY and SAMUEL HARRIS.

As *m*-nitrobenzaldehyde is an important intermediate in the manufacture of certain dyestuffs, it is surprising that there is so little information available on its preparation by the nitration of benzaldehyde. Benzaldehyde was first nitrated by Bertagnini (*Annalen*, 1851, 79, 259), who used both fuming nitric acid and a mixture of nitric and sulphuric acids. He obtained a solid melting at 46°, together with an oil, and oxidised the former to a nitrobenzoic acid which he did not, however, identify. Lippmann and Hawliczek (*Ber.*, 1876, 9, 1463), by adding 1 volume of benzaldehyde to 20 volumes of a mixture of 1 volume of nitric acid and 2 volumes of sulphuric acid, obtained a semi-solid product. After expressing the oil and crystallising the solid residue from alcohol, they obtained a pure compound melting at 58° which they pointed out was *m*-nitrobenzaldehyde and formed the main product of the reaction. They treated the oil with sodium bisulphite solution, extracted the unattacked portion with ether, and distilled it in a vacuum. The distillate on analysis was found to have the same composition as a nitrobenzaldehyde, but they state that oxidation converted it into benzoic acid. This fact taken with its apparent non-reactivity with sodium bisulphite led them to suggest that the oil consisted of benzoyl nitrite, $C_6H_5 \cdot CO \cdot NO_2$. Rudolph (*Ber.*, 1880, 13, 310), however, employing both Bertagnini's and Lippmann and Hawliczek's methods of nitration, found that after shaking the oil with sodium bisulphite solution it yielded on oxidation *o*-nitrobenzoic acid, and expressed the opinion that *o*-nitrobenzaldehyde was present and that this compound did not react with sodium bisulphite. Widman (*Ber.*, 1880, 13, 478), using a nitrating mixture of five volumes of fuming nitric acid and ten volumes of sulphuric acid at a temperature not exceeding 15°, obtained a yield of 70 per cent. of the theoretical amount of pure

m-nitrobenzaldehyde and some 30 per cent. of oil. Friedländer and Henriques (*Ber.*, 1881, 14, 2801), nitrating with a mixture of slightly more than the calculated quantity of potassium nitrate dissolved in concentrated sulphuric acid at a temperature of 30–35°, obtained similar results and confirmed the observation that the oil on oxidation yielded *o*-nitrobenzoic acid; moreover, they showed, contrary to the opinion of Rudolf, that *o*-nitrobenzaldehyde formed a sodium bisulphite compound. Ehrlich (*Ber.*, 1882, 15, 2010) added 100 grams of benzaldehyde to a solution of 110 grams of potassium nitrate in concentrated sulphuric acid at a temperature not exceeding 5° and claims to have obtained a 95 per cent. yield of *m*-nitrobenzaldehyde. He does not, however, state whether this was 95 per cent. of that possible or 95 per cent. of the weight of benzaldehyde used; if the latter, it corresponds to 67 per cent. of theory.

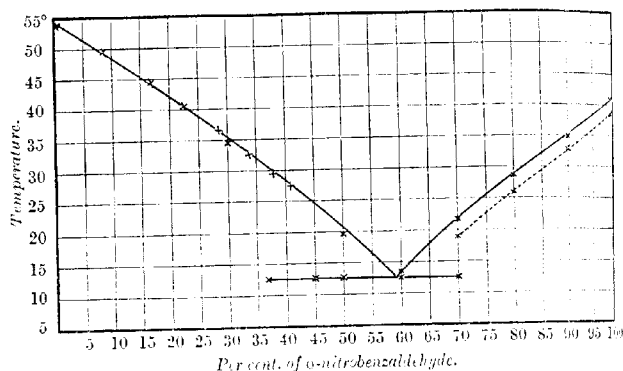
The statement is made in text-books (compare Cain, "Manufacture of Intermediate Products for Dyes," 2nd ed., p. 144) that 20 per cent. of *o*-nitrobenzaldehyde is formed in the nitration of benzaldehyde, the rest being the *m*-isomeride, but there seems to be little published evidence in support thereof. In no case has *o*-nitrobenzaldehyde or a simple derivative been isolated from the nitration product, the only method used for identification being oxidation to *o*-nitrobenzoic acid, a not entirely satisfactory one. However, by partial reduction of technical *m*-nitrobenzaldehyde, reputed to contain 25 per cent. of *o*-nitrobenzaldehyde, with sodium hyposulphite, *o*-aminobenzaldehyde has been isolated in the form of its anhydro-compound, $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}:\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$ (D.R.P. 218364); but again no evidence is forthcoming of the method of determination of the amount of *o*-nitrobenzaldehyde originally present in the technical product, although the patent claims that the yield of the anhydro-aminobenzaldehyde is quantitative.

The problems which presented themselves were, therefore, the detection of *o*-nitrobenzaldehyde, the search for small quantities of *p*-nitrobenzaldehyde, and the determination of the quantities of the isomerides present in the nitration product of benzaldehyde.

Experience shows that the solubility of isomeric organic compounds of closely related constitution frequently decreases with rise in melting point: the phenylhydrazones, therefore, seemed to offer a reasonable prospect of separation of the *o*- from the *m*-nitrobenzaldehyde, as the phenylhydrazone of the former melts some 30° higher than that of the latter and would probably tend to accumulate in the least soluble fraction, the easiest one to isolate. This was found to be the case, and a considerable quantity of the phenylhydrazone of *o*-nitrobenzaldehyde was obtained from the

oil formed in the nitration of benzaldehyde. The phenylhydrazones do not, however, offer a convenient method for the detection of small quantities of *p*-nitrobenzaldehyde in the mixture, as there is little difference between the melting points of the *o*- and *p*-compounds. On the other hand, *p*-nitrobenzaldehyde forms a very sparingly soluble azine of high melting point, so the mixture of azines obtained from the oil was fractionally crystallised. Although *o*-nitrobenzylideneazine was isolated, no evidence of the presence of *p*-nitrobenzylideneazine was obtained. It seems that the product of nitration of benzaldehyde consists essentially of a mixture of *o*- and *m*-nitrobenzaldehydes and that if any *p*-nitrobenzaldehyde is present it is in very small amount.

FIG. 1.



In order to determine the amount of *o*-nitrobenzaldehyde present in the mixture the method of thermal analysis was employed, the binary fusion diagram of *o*- and *m*-nitrobenzaldehydes being constructed (Fig. 1).

Time-cooling curves for pure *o*-nitrobenzaldehyde showed that this compound exists in two forms, the β -, or unstable, form freezing first at 37.9° and the α -, or stable, form afterwards at 40.9°. The phenomena observed on cooling *o*-nitrobenzaldehyde are analogous to those displayed by the mixture of phenol and *p*-toluidine described by Philip (T., 1903, 83, 828), where two forms of the compound of these substances separate (compare also Pickering, T., 1895, 67, 669, who obtained two forms of monochloroacetic acid). Three examples giving the thermometer readings at minute intervals will indicate the behaviour of *o*-nitrobenzaldehyde on cooling from 55°. (1) . . . 41.7°, 40.6°, 39.6°, 38.9°, 38.2°, 37.5°;

37.5°, 37.8°, 37.9°, remains constant for twelve minutes, 38.1°, 38.6°, 38.6°, 39.3°, 40.1°, 40.3°, 40.4°, 40.5°, 40.5°, 40.5°, . . . (2) . . . 41.2°, 39.9°, 39.1°, 38.3°, 37.6°, 37.0°, 36.5°, 36.6°, 37.9°, remains constant for eight minutes, 38.0°, 38.2°, 38.5°, 38.8°, 40.6°, 40.7°, 40.8°, 40.8°, 40.8°, 40.8°, . . . (3) . . . 39.0°, 38.5°, 38.0°, 37.6°, 37.4°, 37.8°, 37.9°, 37.9°, 37.9°, 38.0°, 38.3°, 38.6°, 39.2°, 39.9°, 40.2°, 40.4°, 40.5°, 40.6°, 40.7°, 40.8°, 40.8°, 40.8°, 40.9°, 40.9°, 40.9°, 40.9°, 40.8°, 40.8°, 40.8°. . . Some ten cooling curves were taken and in every case two arrests were observed; the first occurred at 37.8° or 37.9°, but the second was less regular, 40.4° being the minimum and 40.9° the maximum, the higher result being usually obtained if the arrest at the lower temperature was not too prolonged. The longest arrest at the lower temperature was fifteen minutes and the shortest two minutes. The regularity of the results even when different degrees of supercooling occurred seems to remove all possibility that the two arrests were due to the rate of cooling exceeding the rate of liberation of heat during the early stages of crystallisation. When the material, cooled from 55°, was seeded with ordinary *o*-nitrobenzaldehyde at 40°, the temperature continued to fall until it was below the freezing point of the β -form and then rose continuously but very slowly, no arrest occurring at the freezing point of the β -form; the final temperature attained, however, was never quite as high as that observed in the experiments described above. It seems probable that the better results for the freezing point of α -*o*-nitrobenzaldehyde obtained in the former experiments were due to the formation of a covering of the β -form on the walls of the tube which acted as an efficient insulator for the portion remaining unsolidified, whereas when seeding is employed the α -form crystallises very slowly throughout the mass of the liquid.

The unstable β -*o*-nitrobenzaldehyde can be obtained by fusing the aldehyde, cooling rapidly, and scratching with a platinum wire; it melts in a capillary tube at 40° as compared with 43.5° for the stable α -modification. The determination of the melting point was carried out by melting a small quantity of the aldehyde in a capillary tube, care being taken to avoid the presence of nuclei of the compound in the upper part of the tube by warming the whole tube to about 50°; the tube was cooled and crystallisation induced by scratching the liquid with a fine platinum wire. When the solid was formed, the tube was placed in a bath at 35°, and the temperature very cautiously raised, when melting took place at 40°. The tube was then cooled and the liquid inoculated with a very small amount of the stable aldehyde and left for some time; on redetermining the melting point, it was found to have risen to 43.5°.

The β -compound cannot be preserved for any length of time, the change to the α -form starting after a few minutes and being very striking when observed under the microscope. A small quantity of the aldehyde was melted on a slide, cooled, and scratched at the edge with a platinum wire, when crystallisation took place rapidly with the formation of a transparent mass of large crystals, radiating from the point where crystallisation started. After some minutes, one or two nuclei appeared in the form of small, opaque spots which slowly grew and coalesced until the whole material had become opaque. The phenomena could be reproduced by again melting the solid, and centres of change could be started by touching the unstable solid with the α -form. When a thin film of aldehyde was obtained by covering the liquid with a slip and inducing crystallisation as before, long crystals of β -*o*-nitrobenzaldehyde were obtained, radiating from the point of crystallisation. Under these conditions, a somewhat longer period elapsed before the change started (about ten minutes), but when the nuclei had attained some size their growth could be observed as a darker area spreading through the mass. When the change was complete, the original pattern of the crystals remained, but over the whole surface there appeared smaller radiating crystals, of which the longer axes were at an angle to those of the original crystals.

The separation of the two forms of *o*-nitrobenzaldehyde was observed on the ortho-side of the binary fusion diagram, two freezing points being obtained with mixtures containing up to 30 per cent. of *m*-nitrobenzaldehyde. The separation of the β -form is indicated by the broken curve. Considerable difficulty was experienced in determining the freezing points of mixtures of *o*- and *m*-nitrobenzaldehydes containing from 20 to 60 per cent. of the former. There was evidence of the separation of an unstable form of *m*-nitrobenzaldehyde, although cooling curves taken with the pure compound gave no indication of two arrests. With mixtures containing in the neighbourhood of 20 per cent. of *o*-nitrobenzaldehyde, two distinct arrests in the cooling curve were obtained, the first being some 4° lower than the second. The lower arrest was more prolonged if the mixture was melted at 60° and was much less noticeable if the mixture was melted at 55° or seeded with solid *m*-nitrobenzaldehyde. In other cases, however, where mixtures containing more *o*-nitrobenzaldehyde were used, although there was plain indication that two arrests occurred, the temperature at which the first arrest took place was irregular, depending on slight variations in the rate of cooling, stirring, etc.; for this reason the curve for the first arrest has not been plotted. An inspection

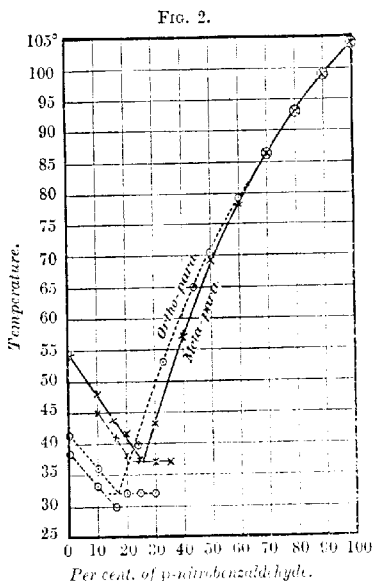
of the mixture containing 19 per cent. of *o*-nitrobenzaldehyde during cooling gave an indication that a change of form took place. A mixture was cooled from 55°; the temperature fell to 34.5° and then rose to 38.3°, where it remained stationary for three minutes; the temperature then fell to 36.9° very slowly, when the mixture was removed from the jacket and examined. It was found that in the translucent, crystalline magma there were floating a number of opaque nuclei; the tube was replaced in the jacket and after two minutes there was a slow rise in temperature, followed by a rapid rise, the final temperature attained being 39.3° as against 42.6°, the highest freezing point obtained for this mixture. The low final temperature was no doubt due to over-cooling. As, however, the appearance of the nuclei described above is the only direct evidence so far obtained of the separation of a second form of *m*-nitrobenzaldehyde, it cannot yet be stated definitely that such a form exists, as the irregularity of the results when more *o*-nitrobenzaldehyde is present suggests that another explanation might be required.

When the amount of *o*-nitrobenzaldehyde was increased to 37.5 per cent., the freezing point of the mixture proved very difficult to determine, and this was the case with all the remaining freezing points on this side of the curve, the values obtained depending on the rate of cooling and the amount of supercooling; seeding did not prove an effective remedy. In the cases of a 45 and a 50 per cent. mixture, no arrest in the cooling curve was obtained until the eutectic point was reached, namely, 12.5°, but having solidified, the mixtures did not completely melt when kept for some days at 18°. It seemed that the difficulty was due to the very slow rate of crystallisation of the *m*-nitrobenzaldehyde with the possible complication of the separation of an unstable form of lower melting point. In order to determine the true freezing points it was necessary to keep the mixtures at constant temperature in a thermostat for six or seven days, seeding every day with a minute amount of *m*-nitrobenzaldehyde. By decreasing the temperature of the thermostat at the end of each week it was possible to find the maximum temperature at which solid separated. The values corresponding with 37.5, 41.5, and 50 per cent. of *o*-nitrobenzaldehyde were obtained in this way. The results from which the curve (Fig. 1) was obtained are given in Table I, the figures in brackets indicating the first arrest, corresponding to the separation of *o*-nitrobenzaldehyde; the first three eutectic temperatures were obtained in the ordinary manner, but the true values for the freezing points corresponding to them were obtained by the thermostat method.

TABLE I.
o- and *m*-Nitrobenzaldehydes.

Per cent. of <i>o</i> -nitrobenz- aldehyde.	Freezing point.	Eutectic temp.	Per cent. of <i>o</i> -nitrobenz- aldehyde.	Freezing point.	Eutectic temp.
0	54.6°		41.5°	27.0°	—
9	49.4		45	—	12.5°
16.7	44.8		50	19.0	12.5
18	43.0		60	12.4	12.3
19	42.6		70	(18.6°) 21.8	12.0
19.5	42.3		80	(26.0) 29.2	
23	40.2		90	(32.2) 34.0	
30	34.4		100	(37.9) 40.9	
37.5	29.2	12.5°			

In the case of the ortho-para and meta-para diagrams (Fig. 2) the separation of two forms of *o*-nitrobenzaldehyde was again



observed and evidence of the separation of an unstable form of *m*-nitrobenzaldehyde was obtained in the cooling curves of mixtures containing 10, 15, and 20 per cent. of *p*-nitrobenzaldehyde; the freezing of the unstable forms is indicated by the dot-and-dash and dash curves, respectively.

Two examples may be given of the behaviour on cooling of mixtures of *m*- and *p*-nitrobenzaldehydes, the temperatures given being taken at one-minute intervals. (1) Mixture containing 10 per cent. of para. . . . 48.0°, 47.0°, 46.4°, 45.2°, 44.2°, 43.7°, 42.9°, 43.6°, 44.0°.

44.2°, 44.4°, 44.7°, 45.0°, 45.1°, 45.2°, 46.0°, 47.1°, 47.6°, 47.8°, 47.9°, 47.8°. . . . (2) Mixture containing 15 per cent. of para. . . . 42.1°, 41.5°, 41.0°, 40.4°, 39.8°, 39.5°, 39.8°, 40.4°, 40.7°, 40.8°, 41.0°, 41.0°, 41.1°, 41.2°, 41.1°, 41.0°, 40.9°, 41.2°, 41.2°, 41.5°, 43.0°, 43.6°, 43.7°, 43.6°, 43.3°. . . . Similarly for mixtures of *o*- and *p*-nitrobenzaldehydes. (1) Mixture containing 10 per

cent. of para. . . . 32.0°, 31.7°, 31.3°, 31.0°, 30.7°, 30.3°, 30.0°, 29.8°, 32.0°, 32.1°, 32.1°, 32.1°, 32.0°, 32.4°, 32.7°, 33.6°, 34.2°, 34.4°, 34.5°, 34.6°, 34.6°, 34.5°, 34.4°. . . . (2) Mixture containing 15 per cent. of para. . . . 29.1°, 28.9°, 28.8°, 28.6°, 28.4°, 28.2°, 28.0°, 27.9°, 27.8°, 27.6°, 27.5°, 27.3°, 27.2°, 27.1°, 27.0°, 26.8°, 26.7°, 26.6°, 26.4°, 26.3°, 29.2°, 29.3°, 29.3°, 29.3°, 29.6°, 29.7°, 29.8°, 32.0°, 32.2°, 32.4°, 32.5°, 32.6°, 32.6°, 32.5°, 32.4°, 32.3°, 32.2°. . . . In some cases, the first arrest is less marked or not obtained at all, and in such circumstances the final freezing point is somewhat higher than that obtained when there is a very marked arrest at the lower temperature.

The results from which the curves in Fig. 2 were constructed are given in Table II, the figures in brackets corresponding to the first arrests due to the separation of unstable forms.

TABLE II.

Per cent. of <i>p</i> -nitrobenz- aldehyde.	Meta-para.		Ortho-para.	
	Freezing point.	Eutectic temp.	Freezing point.	Eutectic temp.
0	54.6°		(37.9°) 40.9°	
10	(44.4°) 46.0		(32.1) 35.2	
15	(41.2)		(29.3) 32.6	
20	(37.5)		34.3	32.2°
25	37.5		38.6	32.0
30	42.9	37.2°	46.4	32.2
35	50.7	37.1	53.0	
40	57.0		—	
45	—		61.6	
50	69.4		70.2	
60	78.3		78.7	
70	86.0		86.0	
80	92.7		92.8	
90	98.8		98.6	
100	104.3		104.3	

The nitration product of benzaldehyde was obtained as described in the experimental section. Two nitrations yielded products freezing at 42.6° and 42.8°, respectively. The mean of these figures, 42.7°, corresponds on the curve to 19 per cent. of *o*-nitrobenzaldehyde. In order to check the accuracy of the curve in this neighbourhood, fresh mixtures were made up containing 18, 19, and 19.5 per cent. of *o*-nitrobenzaldehyde, which were found to freeze at 43.0°, 42.6°, and 42.3°, respectively. In all freezing-point determinations in this neighbourhood two arrests in the cooling curve were obtained; it is imperative, therefore, in order that the second arrest shall not be missed, to prolong the cooling down to room temperature or, better, to seed with *m*-nitrobenzaldehyde from time to time.

By means of the binary fusion diagram it is possible now to

calculate what percentage of the nitration product is liquid at any temperature after an interval to ensure the conversion of the *m*. nitrobenzaldehyde into its stable form; the results for a few temperatures are given in Table III.

TABLE III.

Temp.	40°	35°	30°	25°	20°	15°
Liquid %	82	63	52	45	38	34

It would appear, therefore, that by the nitration of benzaldehyde, followed by expression of the liquid and crystallisation of the product, not much more than a 65 per cent. yield of pure *m*-nitrobenzaldehyde could be hoped for.

EXPERIMENTAL.

Purification of Materials.—A commercial sample of *o*-nitrobenzaldehyde was purified by crystallisation from benzene and light petroleum until the products of two successive crystallisations had the same freezing point. The compound melted at 43.5° in a capillary tube and froze in bulk at 37.9° and 40.9°. Two samples of *m*-nitrobenzaldehyde were used, one a commercial sample, and the other prepared by the nitration of benzaldehyde as described below, followed by expression of the oil. The samples were crystallised from benzene and light petroleum, and in one case from alcohol, until a constant freezing point was obtained. The product from the commercial sample had a green colour when fused, but no difference in freezing point was detected between it and the prepared product; they both melted in a capillary tube at 57.5° and froze in bulk at 54.6°. A commercial sample of *p*-nitrobenzaldehyde was recrystallised from alcohol until a constant freezing point was obtained; the product melted at 106.5° in a capillary tube and froze in bulk at 104.3°.

Nitration of Benzaldehyde.—The nitrating acid was prepared by adding 1560 c.c. of concentrated sulphuric acid to 325 c.c. of fuming nitric acid; on analysis, the mixture was found to contain $\text{H}_2\text{SO}_4 = 83.1$, $\text{HNO}_3 = 13.2$, $\text{HNO}_2 = 0.2$, and $\text{H}_2\text{O} = 3.5$ per cent. The nitrating acid (145 c.c.) was cooled to 0° in ice, and 30 grams of benzaldehyde were added drop by drop with vigorous shaking during twenty to twenty-five minutes, care being taken to avoid rise in temperature. When all the benzaldehyde had been added, the mixture retained a strong odour of that compound, but on removing from the ice and shaking vigorously this soon disappeared and a clear lemon-yellow liquid was obtained. Under these conditions, very little nitrobenzoic acid is produced. The mixture was poured on to crushed ice, and the mother-liquor decanted from the pasty

solid which separated. The paste was then melted under dilute sodium carbonate solution, thoroughly agitated, and the carbonate poured off, these operations being repeated three times. The mixture of nitrobenzaldehydes was finally washed with water and left to solidify. In all these operations care was taken to avoid loss of oil, which might result in change in composition of the mixture. The first washing with sodium carbonate was found to remove practically all the nitrobenzoic acid. As much water as possible was drained off from the solid, which was then melted in a test-tube and the water which separated removed with a pipette. The melted product was poured into a dish and further freed from water by means of filter-paper. Finally, it was poured on to a clock-glass, which was rotated as the liquid cooled in order to spread the solid over a large surface, and then left in an evacuated desiccator over concentrated sulphuric acid for three weeks. The product thus prepared was used for the determination of the freezing point of the nitration mixture. No allowance has been made for any small change in composition of the mixture owing to difference of solubility of the two compounds in the wash-water. Attempts to dry the mixture in a steam-oven demonstrated that at 100° a portion volatilised, and decomposition also took place, the freezing point of the product falling with increased period of heating. For the examination of the liquid product of nitration the mixture of nitrobenzaldehydes was prepared as above, but, after washing, it was allowed to solidify under water. The solid was pressed in a Buchner funnel and the oil sucked off by means of a water-pump.

Examination of the Oil.—Seventeen grams of the oil obtained as above were dissolved in 75 c.c. of boiling alcohol and treated with 15 grams of phenylhydrazine; after a few minutes a considerable precipitate appeared, which, after separation from the hot solution and washing with alcohol, was found to melt at 151° and when mixed with *o*-nitrobenzaldehydephenylhydrazone (m. p. 153°) at 153°. One crystallisation of this from alcohol gave pure *o*-nitrobenzaldehydephenylhydrazone. Ten grams of the oil, dissolved in 50 c.c. of boiling alcohol, were treated with 3 grams of 50 per cent. hydrazine hydrate solution. The azine began to separate and as *p*-nitrobenzylidenazine is almost insoluble in alcohol the solution was filtered while hot and the solid fractionally crystallised; *o*-nitrobenzylidenazine (m. p. 204°) was isolated, but nothing of a higher melting point. The alcoholic solution on cooling deposited more of the azine, but on fractional crystallisation no indication of the presence of the high-melting *p*-nitrobenzylidenazine (m. p. 206°) was obtained.

Determination of Freezing Points.—The freezing points were read

from the cooling curves. The apparatus employed consisted of a small silica test-tube, containing the mixture, jacketed with a cylindrical Dewar vessel fitting fairly closely. A tightly fitting cork in the silica tube carried a stirrer of stout platinum wire and a thermometer, which was of the small-bulb, Anschütz type and standardised. The exposed column of the thermometer was short and no correction has been applied. From 5—10 grams of material were used for each determination.

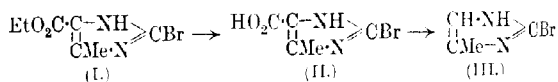
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UNIVERSITY COLLEGE, LONDON. [Received, November 28th, 1922.]

LXII.—Bromo-derivatives of 4-Methylglyoxaline.

By FRANK LEE PYMAN and GEOFFREY MILLWARD TIMMIS.

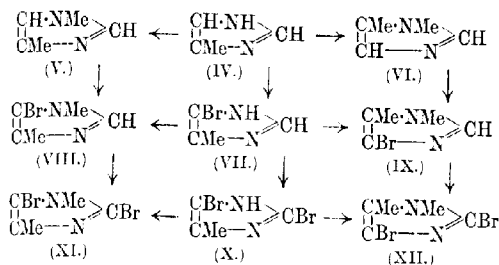
THE bromination of 4-methylglyoxaline (IV) has been shown (Pyman, T., 1910, 97, 1814) to lead to the formation of 2:5-dibromo-4-methylglyoxaline (X) together with 2(or 5)-bromo-4-methylglyoxaline, in which the position of the bromine atom was undetermined. It is now shown that this is 5-bromo-4-methylglyoxaline (VII), since it is not identical with 2-bromo-4-methylglyoxaline (III) which has been prepared synthetically. The method employed for the synthesis was the bromination of ethyl 4-methylglyoxaline-5-carboxylate (Gerngross, *Ber.*, 1912, 45, 524) with the formation of *ethyl 2-bromo-4-methylglyoxaline-5-carboxylate* (I), hydrolysis of the ester to the corresponding *acid* (II), and decarboxylation of the latter by heating with water at 150°, when 2-bromo-4-methylglyoxaline was obtained.



The constitution of this base is confirmed by the fact that it yields on nitration 2-bromo-5-nitro-4-methylglyoxaline (XV), identical with the bromination product of 5-nitro-4-methylglyoxaline described by Windaus (*Ber.*, 1909, 42, 758). 2-Bromo-4-methylglyoxaline is readily reduced to 4-methylglyoxaline by means of sodium sulphite, and yields 2:5-dibromo-4-methylglyoxaline on bromination.

The determination of the constitutions of 5-bromo-4-methylglyoxaline and of 1:4- and 1:5-dimethylglyoxalines (Pyman, T., 1922, 121, 2616) establishes the constitutions of the bromo- and dibromo-dimethylglyoxalines previously described (T., 1910, 97,

1814), for the bromination of 1:4- and 1:5-dimethylglyoxalines (V and VI) gave a mixture of mono- and di-bromoglyoxalines, which were also obtained by the methylation of 5-bromo-4-methylglyoxaline and 2:5-dibromo-4-methylglyoxaline, and therefore must have the constitutions represented by the formulæ VIII, IX, XI, XII.

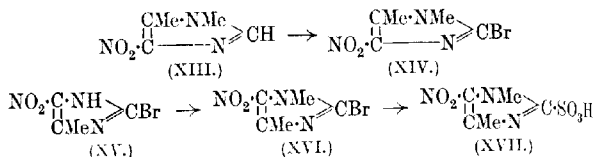


Knowledge of the constitutions of these compounds, of the nitrodimethylglyoxalines (Pyman, T., 1922, 121, 2616), and of the bromonitrodimethylglyoxalines, described in this paper, permits an explanation of some of their reactions based on the mutual influence of the substituent groups and the fact that the conjugated system connecting the 2- and 5-carbon atoms of the glyoxaline ring is similar* to the conjugated para-linking in the benzene nucleus.

Thus, it was pointed out previously that the bromination of 1:4- and 1:5-dimethylglyoxalines with 1 mol. of bromine under the same conditions led to different results, the first yielding chiefly 5-bromo-1:4-dimethylglyoxaline (VIII) with little 2:5-dibromo-1:4-dimethylglyoxaline (XI), whilst the second gave very little 4-bromo-1:5-dimethylglyoxaline (IX), but chiefly 2:4-dibromo-1:5-dimethylglyoxaline (XII). This result may be explained by the superior para-directive power of the methyl group in 4-bromo-1:5-dimethylglyoxaline as compared with that of the bromine atom in 5-bromo-1:4-dimethylglyoxaline. It has been found, however, that bromination of 5-bromo-1:4-dimethylglyoxaline and 4-bromo-1:5-dimethylglyoxaline with 1 mol. of bromine leads to the corresponding dibromo-derivatives in good yield. The earlier results, therefore, only show that 1:4-dimethylglyoxaline is brominated more readily than its 5-bromo-derivative, whilst 1:5-dimethylglyoxaline is brominated less readily than 4-bromo-1:5-dimethylglyoxaline. The relative directive properties of

* Evidence of this similarity is afforded by the rearrangement of the benzidine type, which takes place on the reduction of 2-arylazoglyoxalines (Fargher and Pyman, T., 1919, 115, 222).

substituents in the 4- and 5-positions are, however, well illustrated by the bromination of the nitrodimethylglyoxalines. 4-Nitro-1:5-dimethylglyoxaline (XIII) readily yields 2-bromo-4-nitro-1:5-dimethylglyoxaline (XIV), the 2-position being para to the methyl and meta to the nitro-group, whilst no trace of 2-bromo-5-nitro-1:4-dimethylglyoxaline (XVI) could be obtained by the bromination of 5-nitro-1:4-dimethylglyoxaline, in which the 2-position is para to the nitro-group and meta to the methyl group



2-Bromo-5-nitro-1:4-dimethylglyoxaline was readily prepared by the methylation of 2-bromo-5-nitro-4-methylglyoxaline (XV), none of the isomeric 2-bromo-4-nitro-1:5-dimethylglyoxaline being isolated from the products of reaction. This result is similar to that obtained in the methylation of 5-nitro-4-methylglyoxaline (T., 1922, 121, 2616). The bromine atom in 2-bromo-5-nitro-1:4-dimethylglyoxaline, being para to a nitro-group, is readily replaced by the sulphonic acid residue, for on boiling with one mol. of aqueous sodium sulphite for three hours it gives an excellent yield of 5-nitro-1:4-dimethylglyoxaline-2-sulphonic acid (XVII), whereas the isomeric 2-bromo-4-nitro-1:5-dimethylglyoxaline is much less readily attacked by sodium sulphite under the same conditions, for 40 per cent. was recovered unchanged, no 4-nitro-1:5-dimethylglyoxaline was formed, and the remainder was converted into products which were not characterised. The behaviour of 2-bromo-5-nitro-4-methylglyoxaline towards sodium sulphite resembles that of 2-bromo-4-nitro-1:5-dimethylglyoxaline, and not that of 2-bromo-5-nitro-1:4-dimethylglyoxaline, which is the principal product of its methylation. This fact accords well with the view of the alkylation of amidines recently expressed by one of us in conjunction with Burtles (this vol., p. 363).

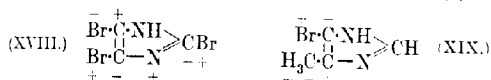
The action of hot aqueous sodium sulphite on other bromo-derivatives of 4-methylglyoxaline is described in the experimental part of the paper. The results combined with those obtained by one of us in collaboration with Balaban (T., 1922, 121, 947) and Light (T., 1922, 121, 2626) lead to the following general conclusions:

(1) In the case of glyoxalines containing a free imino-group, a bromine atom in the 2-position is readily replaced by hydrogen (except in the case of 2-bromo-5-nitro-4-methylglyoxaline), and one

of two bromine atoms situated in the 4- and 5-positions with less readiness; a single bromine atom in the 4-position is stable to the reagent in 4-bromoglyoxaline or 4-bromo-2-methylglyoxaline, but is capable of replacement by hydrogen when a methyl group occupies the 5-position; replacement of bromine by the sulphonic acid residue has been observed only in the case of 2:4:5-tribromoglyoxaline, when 4-bromoglyoxaline-5-sulphonic acid is obtained.

(2) In *N*-methylglyoxalines, bromine atoms in the 2-position are much less readily replaced by hydrogen, for 2:5-dibromo-1:4-dimethylglyoxaline is only slowly, and 2:4-dibromo-1:5-dimethylglyoxaline not perceptibly, attacked by prolonged boiling with aqueous sodium sulphite: halogen atoms in the 2-position of *N*-methylglyoxalines readily suffer the replacement of halogen by the sulphonic acid residue when the 5-position is occupied by a group of strong positive polarity, for example, in the case of 2-bromo-5-nitro-1:4-dimethylglyoxaline quoted above, and the case of 8-chlorocaffeine (D.R.-P. 74045; compare Pyman, this vol., p. 369).

These results may be partly explained in the light of Lapworth's view (*Mem. Manchester Phil. Soc.*, 1920, 64, ii, 8; Lapworth and Shoesmith, T., 1922, 121, 1394) that the mode of replacement of a bromine atom is influenced by its induced polarity. For instance, representation of the alternate polarities of 2:4:5-tribromoglyoxaline by the formula (XVIII) corresponds with the facts (1) that the



2- and 4-bromine atoms are readily replaced by hydrogen, and (2) that the 5-bromine atom may be replaced by the sulphonic acid residue, whilst the reducibility of 5-bromo-4-methylglyoxaline (XIX) may be ascribed to positive polarity of the bromine atom induced by the methyl group.

EXPERIMENTAL.

Bromination of Ethyl 4-Methylglyoxaline-5-carboxylate.—To 7.5 grams of ethyl 4-methylglyoxaline-5-carboxylate (Gerngross, *Ber.*, 1912, 45, 524) in 100 c.c. of chloroform, a solution of 2.5 c.c. of bromine in 50 c.c. of chloroform was added, the solution being cooled with ice-water. The mixture was distilled with steam until the free bromine and chloroform had been removed, and the resulting aqueous solution was cooled and mixed with a limited quantity of concentrated aqueous sodium carbonate so that it remained just acid to methyl-orange, when 3.5 grams of ethyl 2-bromo-4-methylglyoxaline-5-carboxylate separated as a white, crystalline powder

melting at 152—153°. The mother-liquor was treated with a further quantity of sodium carbonate and deposited 4.4 grams of crystalline material, melting at 175—200°, which consisted chiefly of unbrominated ester, and gave on repeating the above bromination process a further quantity of 2.4 grams of the bromo-ester, melting at 152—153°. The total yield of this, 5.9 grams, is 52 per cent. of the theoretical.

Ethyl 2-bromo-4-methylglyoxaline-5-carboxylate crystallises from water in long, colourless needles which melt to a colourless liquid at 153° (corr.) (Found: C = 36.2; H = 3.8; N = 11.8; Br = 34.5. $C_7H_9O_2N_2Br$ requires C = 36.0; H = 3.9; N = 12.0; Br = 34.3 per cent.). It is soluble in about 36 parts of boiling water and 275 parts of cold water, very easily soluble in alcohol or chloroform, and easily soluble in ether.

It is readily soluble in cold dilute mineral acids or alkalis, including sodium carbonate.

Hydrolysis.—Five grams of the bromo-ester were boiled with 75 c.c. of 20 per cent. hydrochloric acid for two hours under reflux, and concentrated aqueous sodium carbonate was then added until the solution was only faintly acid to methyl-orange, when 4.0 grams of the bromo-acid were obtained in a pure state, that is, 91 per cent. of the theoretical yield.

2-Bromo-4-methylglyoxaline-5-carboxylic acid crystallises from glacial acetic acid in colourless, prismatic rods which melt and decompose at temperatures varying considerably with the conditions of heating. Placed in a bath at 220°, and heated slowly, it melts and decomposes at about 234° (corr.) (Found: C = 29.4; H = 2.5; N = 13.9; Br = 38.8. $C_5H_5O_2N_2Br$ requires C = 29.4; H = 2.4; N = 13.7; Br = 39.0 per cent.).

It is very sparingly soluble in water and sparingly soluble in the usual organic solvents. It is readily soluble in dilute mineral acids or alkalis, including sodium carbonate.

2-Bromo-4-methylglyoxaline.

Two grams of 2-bromo-4-methylglyoxaline-5-carboxylic acid and 20 c.c. of water were heated for three and a half hours at 150°. On cooling, the solution deposited 1.2 grams of crude 2-bromo-4-methylglyoxaline, melting at 118°, that is, 76 per cent. of the theoretical yield. After recrystallisation from water, this has formed colourless, glistening needles which melted at 124—125° (corr.) (Found: C = 30.1; H = 3.1; N = 17.6; Br = 49.9. $C_4H_5N_2Br$ requires C = 29.8; H = 3.1; N = 17.4; Br = 49.7 per cent.).

2-Bromo-4-methylglyoxaline is soluble in about 15 parts of boiling

water and sparingly soluble in cold water, giving a solution faintly alkaline to litmus. It is very easily soluble in alcohol, fairly easily soluble in ether or chloroform, more sparingly soluble in benzene, and almost insoluble in light petroleum. It dissolves readily in dilute mineral acids or in aqueous sodium hydroxide or ammonia, but not in aqueous sodium carbonate.

The *picrate* crystallises from water in primrose-yellow needles which melt at $172\text{--}173^\circ$ (corr.), and are sparingly soluble in cold water.

Reduction by Sodium Sulphite.—0.4 Gram of 2-bromo-4-methylglyoxaline was boiled with a solution of 0.65 gram of hydrated sodium sulphite (1 mol.) in 2.6 c.c. of water for three hours under reflux. On the addition of cold saturated aqueous picric acid, 0.46 gram of 4-methylglyoxaline *picrate* separated at once, and a second crop of 0.12 gram was obtained on concentration of the mother-liquor. Both crops melted at $160\text{--}161^\circ$ (corr.), alone or mixed with a specimen of the *picrate* prepared from 4-methylglyoxaline. The yield is thus 75 per cent. of the theoretical.

Bromination. 0.2 Gram of 2-bromo-4-methylglyoxaline was treated with 0.1 c.c. of bromine in chloroform solution, and after removal of the solvent the residue was digested with 5 c.c. of warm water. 0.25 Gram of crude 2:5-dibromo-4-methylglyoxaline, melting at 219° , remained undissolved, and after crystallisation from ethyl acetate melted at $214\text{--}215^\circ$ (corr.), alone or mixed with a specimen from another source.

Nitration. To 1 gram of 2-bromo-4-methylglyoxaline cooled with ice, there were added first 0.5 c.c. of concentrated nitric acid, and then 2 c.c. of concentrated sulphuric acid. After keeping over-night, the clear solution was poured into water, when 0.9 gram of 2-bromo-5-nitro-4-methylglyoxaline was precipitated, that is, 70 per cent. of the theoretical yield. The crude product melted at 219° , and after recrystallisation from water formed glistening needles which melted at $220\text{--}221^\circ$ (corr.), alone or mixed with the bromination product of 5-nitro-4-methylglyoxaline (compare p. 501).

Coupling.—2-Bromo-4-methylglyoxaline gives a tawny yellow precipitate with *p*-bromobenzenediazonium chloride in the presence of sodium carbonate, and gives a clear brownish-yellow solution with sodium diazobenzene-*p*-sulphonate in the presence of either sodium hydroxide or carbonate. The isomeric 5-bromo-4-methylglyoxaline, on the other hand, gives with sodium diazobenzene-*p*-sulphonate, a deep red solution in the presence of sodium carbonate but a brownish-yellow solution in the presence of sodium hydroxide.

5(4)-Bromo- and 2 : 5(4)-Dibromo-derivatives of 4-Methyl- and 1 : 4- and 1 : 5-Dimethyl-glyoxalines.

Volatility of the Bromodimethylglyoxalines.—The mono- and di-bromo-derivatives of 1 : 4- and 1 : 5-dimethylglyoxalines can be distilled unchanged under 10 mm. approximately at the following temperatures : 5-bromo-1 : 4-dimethylglyoxaline 168°; 2 : 5-dibromo-1 : 4-dimethylglyoxaline 130°; 4-bromo-1 : 5-dimethylglyoxaline 160°; 2 : 4-dibromo-1 : 5-dimethylglyoxaline 175°.

Bromination of 5-Bromo-1 : 4-dimethylglyoxaline and 4-Bromo-1 : 5-dimethylglyoxaline.—3·5 Grams of each base were dissolved in 17 c.c. of chloroform, mixed with a solution of 1 c.c. of bromine in 5 c.c. of chloroform, kept for an hour, and then worked up for the dibromo-derivatives by methods sufficiently indicated in the previous paper (T., 1910, 97, 1831).

There were thus obtained from 5-bromo-1 : 4-dimethylglyoxaline 2·6 grams of pure 2 : 5-dibromo-1 : 4-dimethylglyoxaline and from 4-bromo-1 : 5-dimethylglyoxaline 3·7 grams of pure 2 : 4-dibromo-1 : 5-dimethylglyoxaline.

Reduction by Sodium Sulphite.—The bromo-compounds (3 grams) were boiled under reflux with hydrated sodium sulphite dissolved in 4 parts of water, using either 1 mol. of sulphite for three hours (conditions A) or 2 mols. of sulphite for six hours (conditions B). The methods of separating the mono- and di-bromo-derivatives were essentially those described previously (T., 1910, 97, 1814), whilst the separation of 4-methylglyoxaline from its bromo-derivatives depends on its greater solubility in water and smaller solubility in ether, and its isolation as picrate. The results were as follows, the yields being expressed in percentages of the theoretical : 5-Bromo-4-methylglyoxaline gave under conditions A, 82·3 per cent. unchanged and 14·3 per cent. of 4-methylglyoxaline; under conditions B, 45·3 per cent. unchanged and 51·0 per cent. of 4-methylglyoxaline.

2 : 5-Dibromo-4-methylglyoxaline gave under conditions A 41·6 per cent. unchanged, 38·4 per cent. of 5-bromo-4-methylglyoxaline, and 12 per cent. of 4-methylglyoxaline.

2 : 5-Dibromo-1 : 4-dimethylglyoxaline was treated under conditions B except that owing to its ready volatility with steam it was heated with aqueous sulphite under pressure at 102°, the boiling point of 20 per cent. aqueous sodium sulphite, instead of being boiled under reflux : 90 per cent. was recovered unchanged and 4·6 per cent. reduced to 5-bromo-1 : 4-dimethylglyoxaline. 4-Bromo-1 : 5-dimethylglyoxaline and 2 : 4-dibromo-1 : 5-dimethylglyoxaline were recovered unchanged to the extent of 98·6 and 99·3 per cent. respectively after treatment under conditions B.

The Bromonitrodimethylglyoxalines.

2-Bromo-5-nitro-4-methylglyoxaline was prepared by treating 15 grams of 5-nitro-4-methylglyoxaline with 9 c.c. of bromine, cooling the mixture in cold water. The product was crystallised from boiling water, when 13.5 grams of the pure substance were obtained, that is, 55 per cent. of the theoretical yield. It crystallised from water in glistening needles which melted at $220-221^{\circ}$ (corr.), solidified on cooling, and on reheating melted again at the same temperature, then gradually darkened and decomposed at about 240° . Windaus (*loc. cit.*), who also prepared the compound by the action of bromine on 5-nitro-4-methylglyoxaline, stated that it crystallised from water in fan-shaped prisms, which melted and decomposed at about 228° , and gave the results of satisfactory estimations of nitrogen and bromine. In view of the divergence of our observations from those of Windaus, our product was also subjected to analysis, when it gave satisfactory results (Found: C = 23.0; H = 2.3; N = 20.6; Br = 39.2. Calc., C = 23.3; H = 1.9; N = 20.4; Br = 38.8 per cent.).

We then communicated with Professor Windaus, who kindly re-examined the substance and substantially confirmed our observations.

2-Bromo-5-nitro-4-methylglyoxaline is soluble in about 35 parts of hot water or 300 parts of cold water, easily soluble in alcohol, somewhat sparingly soluble in ether, and very sparingly soluble in chloroform. It is soluble in a large excess of 5N-hydrochloric acid, but dissolves readily in aqueous sodium hydroxide or carbonate or ammonia, giving yellow solutions.

Action of Sodium Sulphite.—Five grams dissolved in a hot solution of 7.5 grams of hydrated sodium sulphite in 30 c.c. of water, giving a yellow solution, but after boiling for six hours under reflux, 1.8 grams were recovered unchanged, and no other organic products could be isolated from the mother-liquor.

Methylation of 2-Bromo-5-nitro-4-methylglyoxaline.—A mixture of 7.5 grams of 2-bromo-5-nitro-4-methylglyoxaline and 3.5 c.c. of methyl sulphate was heated in boiling water. After a few minutes, reaction took place, the mixture becoming liquid and deep reddish-brown in colour, whilst some acrid gas, probably hydrogen bromide, was evolved. The heating was continued for half an hour, and the product mixed with water and excess of sodium carbonate and cooled, when 4.4 grams of slightly sticky, yellow crystals, which melted at about 60° , were obtained. After one crystallisation from ether, 3.7 grams of nearly pure 2-bromo-5-nitro-1:4-dimethylglyoxaline, melting at $64-65^{\circ}$, were obtained. The aqueous

mother-liquor gave on extraction with chloroform 1.5 grams of a yellow oil, which deposited 0.2 gram of the crystalline substance melting at 65° , and finally gave 0.3 gram of unchanged 2-bromo-5-nitro-4-methylglyoxaline after neutralisation with sulphuric acid.

2-Bromo-5-nitro-1:4-dimethylglyoxaline was thus obtained in a yield of 49 per cent. of the theoretical. It distils at 162° under 10 mm. as a pale yellow oil, which quickly solidifies, and crystallises from alcohol in large, nearly colourless prisms which have a very pale greenish-yellow tinge and melt at $67-68^{\circ}$ (corr.) (Found: C = 27.4; H = 2.7; N = 19.2; Br = 36.3. $C_5H_6O_2N_3Br$ requires C = 27.3; H = 2.7; N = 19.1; Br = 36.4 per cent.). It is very sparingly soluble in water, but easily soluble in alcohol, ether, or chloroform. It is insoluble in cold aqueous sodium hydroxide, but dissolves easily in 5N-hydrochloric acid, and the solution on concentration and cooling deposits the *hydrochloride* in colourless prisms which melt and decompose at 187° (corr.). This salt dissociates on treatment with water.

Action of Sodium Sulphite.—Two grams of 2-bromo-5-nitro-1:4-dimethylglyoxaline were boiled under reflux with a solution of 2.3 grams of hydrated sodium sulphite in 13.2 c.c. of boiling water, and passed into solution in the course of fifteen minutes. After boiling for three hours, the solution was cooled and mixed with 5 c.c. of concentrated hydrochloric acid, when 1.6 grams of the sulphonic acid separated, that is, 76 per cent. of the theoretical yield.

5-Nitro-1:4-dimethylglyoxaline-2-sulphonic acid crystallises from water in colourless, diamond-shaped plates, which contain $\frac{1}{2}H_2O$, and melt and decompose at 293° (corr.) after darkening from about 280° [Found: in air-dried substance, loss at 120° = 4.2; S = 14.0 (by fusion with Na_2O_2). $C_5H_7O_5N_3S, \frac{1}{2}H_2O$ requires H_2O = 3.9; S = 13.9 per cent. Found: in substance dried at 120° , C = 27.0; H = 3.3; N = 19.0 (Kjeldahl). $C_5H_7O_5N_3S$ requires C = 27.1; H = 3.2; N = 19.0 per cent.]. It is readily soluble in hot water, giving a solution strongly acid to litmus. Its solution in excess of sodium hydroxide (but not sodium carbonate or ammonia) rapidly becomes burgundy-red in colour.

Bromination of 4-Nitro-1:5-dimethylglyoxaline.—To 2.8 grams of 4-nitro-1:5-dimethylglyoxaline, partly dissolved in 28 c.c. of chloroform, a solution of 1.0 c.c. of bromine in 10 c.c. of chloroform was added. After keeping for a few minutes, 14 c.c. of water were added, and the mixture was heated on the water-bath to remove chloroform and the excess of bromine, when a crystalline solid separated from the aqueous solution. This was crystallised from water, the earlier crops giving 2.1 grams of pure 2-bromo-4-nitro-

1:5-dimethylglyoxaline, that is, 48 per cent. of the theoretical yield, whilst the mother-liquors deposited 0.65 gram of slightly impure 4-nitro-1:5-dimethylglyoxaline, melting at 155°.

2-Bromo-4-nitro-1:5-dimethylglyoxaline crystallises from water in microscopic needles which melt at 179–180° (corr.), and resolidify on cooling. It distils at 227°/10 mm. with slight discoloration (Found: C = 27.4; H = 2.7; N = 19.3; Br = 36.3. $C_6H_6O_2N_3Br$ requires C = 27.3; H = 2.7; N = 19.1; Br = 36.4 per cent.). It dissolves in about 100 parts of boiling water and in about 1000 parts of cold water. It is sparingly soluble in cold alcohol or ether, easily soluble in chloroform, and insoluble in cold aqueous sodium hydroxide. It is more soluble in 5N-hydrochloric acid than in water, but on cooling a hot solution the base separates.

Action of Sodium Sulphite.—1.5 Grams was not completely dissolved on boiling with 1.75 grams of hydrated sodium sulphite in 10 c.c. of water for six hours under reflux, and 0.6 gram was recovered unchanged, whilst the mother-liquors gave on concentration 0.15 gram of glistening, colourless needles, which appeared on qualitative examination to be the sodium salt of a sulphonic acid.

Bromination of 5-Nitro-1:4-dimethylglyoxaline.—This experiment was carried out several times under the conditions employed in the case of 4-nitro-1:5-dimethylglyoxaline. On working up the products, 60 per cent. of the 5-nitro-1:4-dimethylglyoxaline was recovered unchanged and a little bromoform was obtained, together with very small quantities of other compounds which were not obtained in a pure state. A careful search failed to reveal the presence of any 2-bromo-5-nitro-1:4-dimethylglyoxaline.

The authors are indebted to the Wellcome Chemical Research Laboratories for a part of the material employed in this investigation.

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[Received, February 14th, 1923.]

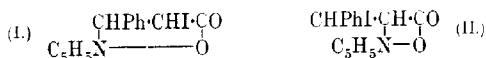
LXIII.—*The Formation of Quaternary Ammonium Salts. Part I.*

By EDWARD DE BARRY BARNETT, JAMES WILFRED COOK, and
ERNEST PERCY DRISCOLL.

In previous communications (Barnett and Cook, T., 1921, 119, 991; 1922, 121, 1376; Barnett, Cook, and Grainger, *ibid.*, 1922, 121, 2059) it has been shown that pyridinium salts can often be obtained directly by the simultaneous action of pyridine and

bromine on certain organic compounds. Considerable interest attaches to the reaction not only from a purely scientific point of view, but also from the possible technical application of the products, and therefore we decided to undertake a systematic investigation of the conditions requisite for the direct formation of quaternary salts. Up to the present we have confined ourselves to pyridinium salts, as pyridine is readily available in large amounts and has proved to be particularly suited to our purpose, but we intend to extend our investigations to the formation of quaternary salts from other tertiary bases.

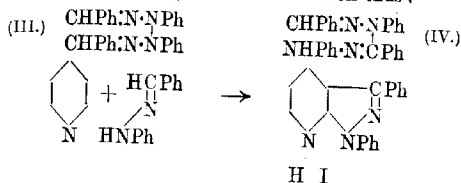
Direct quaternary salt formation by treatment with pyridine and a halogen can take place with compounds containing a hydrogen atom which is readily replaceable by a halogen atom. Thus Ortoleva (*Gazzetta*, 1900, **30**, i, 509) obtained a betaine by treating malonic acid with iodine in pyridine solution, the formation of this compound obviously being due to the intermediate formation of iodomalonic acid. Somewhat similar to this type of reaction is the direct formation of a quaternary salt by treating an unsaturated compound with a halogen in pyridine solution. As an example of this may be cited the formation of a betaine (I or II) by treating cinnamic acid with iodine and pyridine (Ortoleva, *Gazzetta*, 1899, **29**, i, 503):



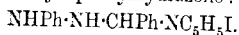
The ease with which these reactions take place is remarkable when it is remembered with what difficulty iodine usually enters into addition and substitution reactions. The explanation probably lies in the formation of a loose compound of iodine and pyridine, and we hope to investigate this reaction in greater detail in the near future, as there seems to be considerable probability of utilizing it for the quantitative estimation of unsaturated groups. Since the "bridge" bond in anthracene closely resembles a double bond in its behaviour, the formation of 9:10-dihydroanthraquinylidipyridinium dibromide (Barnett and Cook, *loc. cit.*) from anthracene, pyridine, and bromine is probably to be classed as quaternary salt formation from an unsaturated compound, but in this case the reaction does not take place if iodine is substituted for bromine.

The formation of pyridinium salts from unsaturated compounds does not seem to be confined to those in which the double bond lies between two carbon atoms. Thus Ortoleva (*Gazzetta*, 1903, **33**, 51; *Atti R. Accad. Lincei*, 1903, [v], **16**, i, 874) treated benzaldehydephenylhydrazone with iodine in pyridine solution, and,

in addition to the oxidation products (III and IV), obtained a third substance which melted at 265–267°. This he regarded as a pyridinopyrazole and explained its formation thus :



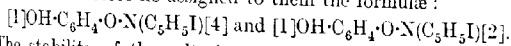
but it is very improbable that replacement of the hydrogen atoms of the pyridine ring would take place under the experimental conditions employed, and it is much more probable that the compound was a pyridinium salt formed by the addition of pyridine hydriodide to benzaldehydephenylhydrazone :



This formula is in agreement with the analyses given by Ortoleva, but the reaction requires further investigation.

The last class of compounds which have been found to be capable of direct quaternary salt formation comprises those containing the quinonoid group, and the present communication deals with this reaction. Up to the present we have confined our experiments to those compounds in which the quinonoid grouping is due to two cyclic carbonyl groups, but preliminary work has been carried out with other quinonoid derivatives and it seems probable that the reaction is a general one.

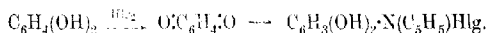
Ortoleva (*Gazzetta*, 1901, **31**, ii, 256; 1902, **32**, i, 447), by treating quinol or catechol with pyridine and iodine, obtained water-soluble iodides. He also found that benzoquinone and pyridine hydriodide gave the same product as was obtained from quinol, pyridine, and iodine. As his salts had no ketonic properties and as he was only able to obtain monoacetyl derivatives, Ortoleva concluded that in them the pyridinium group must be attached to an oxygen atom, and therefore he assigned to them the formulæ :



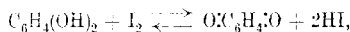
The stability of the salts is not in accord with these formulæ, and two of us have already had cause to criticise them adversely (Barnett and Cook, *loc. cit.*). It was therefore decided to repeat and extend Ortoleva's experiments, and in the present communication it will be shown conclusively that the above formulæ are erroneous, and that the compounds are really dihydroxyphenylpyridinium salts. The main proof of the presence of the two hydroxyl groups rests on the fact that we have been able to pre-

pare diacetates, in contradiction to Ortoleva's assertion that only monoacetyl derivatives can be obtained.

Since only those phenols in which there are two hydroxyl groups in the ortho- or para-position to one another give pyridinium salts when treated with pyridine and a halogen, it is reasonably certain that the first step in the reaction consists in oxidation to a quinone, so that the mechanism of the reaction is essentially the same whether the preparation is carried out from the dihydric phenol, pyridine, and a halogen, or from the quinone and pyridine hydrohalide.

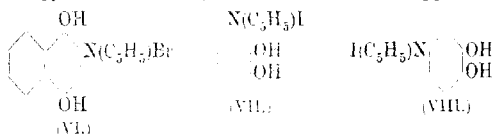


At first it seems strange that this reaction should take place at all when the halogen used is iodine, as a method for the quantitative estimation of quinones has been based on their reduction by hydriodic acid (Valeur, *Compt. rend.*, 1899, 129, 552; Willstätter and Majima, *Ber.*, 1910, 43, 1171). The reaction between iodine and the dihydric phenol, however, is no doubt a reversible one,



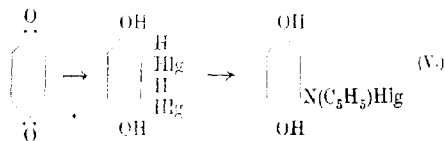
and only takes place to an appreciable extent from left to right so long as the hydriodic acid is removed by conversion into pyridine hydriodide, and addition of this to the quinone, but up to the present we have not investigated the physical chemistry of the reaction.

In the case of quinol there is no alternative formula possible for the pyridinium salt (V) and the same remark applies to the



corresponding bromide obtained from 1:4-naphthaquinone and pyridine hydrobromide (VI). In the case of catechol the salt may be represented by VII or VIII and we have been unable to decide which of these is correct.

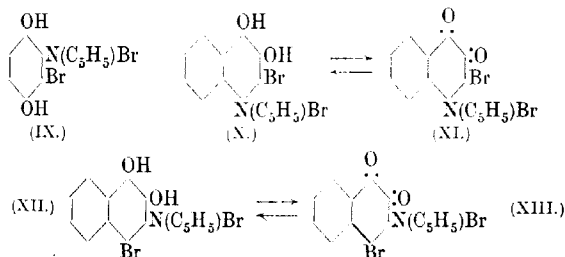
At first it seemed probable that the formation of these mono-pyridinium salts was due to the addition of halogen acid to the quinone and subsequent pyridinium salt formation and enolisation.



If this were the case, the reaction should be confined to the halogen acids, but Ortoleva (*Gazzetta*, 1903, **33**, i, 164) has found that the corresponding nitrate is formed from benzoquinone, pyridine, and nitric acid, and we have confirmed his observations in this respect and have found that sulphuric acid acts in the same way. Indeed it will be shown in a future communication that the reaction can be applied to a large number of acids. As it is extremely improbable that benzoquinone and nitric or sulphuric acid would form a compound by addition that would undergo quaternary salt formation, we have been forced to the conclusion that these salts are formed by the direction addition of the pyridine salt to the quinone.

In the dihydroxyphenylpyridinium salts mentioned above the hydroxyl groups are still in the ortho- or para-position with reference to one another. These compounds should therefore be capable of oxidation to the corresponding quinonepyridinium salt, which might then unite with a second molecule of a pyridine salt to produce a dihydroxyphenyldipyridinium compound. Our experiments have shown that this is actually the case, although the resulting compounds are unstable and the excessive solubility of the dipyridinium salts renders them almost impossible to isolate.

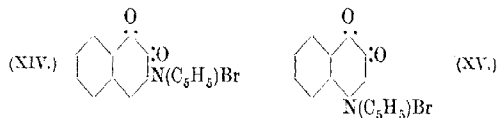
The treatment of a quinone dibromide with pyridine might lead to several products owing to the possibility of enolisation and loss of hydrogen bromide taking place, with or without the simultaneous formation of a quaternary salt. In the case of *p*-benzoquinone dibromide, treatment with pyridine leads to the production of a compound which is almost certainly bromoquinolpyridinium bromide (IX), although it is exceedingly difficult to purify and all the samples prepared showed a slight deficiency in bromine. A similar reaction takes place when 1:2-naphthaquinone dibromide is treated with pyridine, the product being a bromodihydroxy-naphthalenepyridinium bromide (X or XII).



If the reaction is carried out in the presence of excess of bromine, the corresponding quinone (XI or XIII) is obtained, and this can be

reduced to the dihydroxy-compound by sulphurous acid. The isolation in this case of both the quinone and the dihydroxy-compound furnishes the necessary proof that enolisation has taken place during the formation of the pyridinium salt.

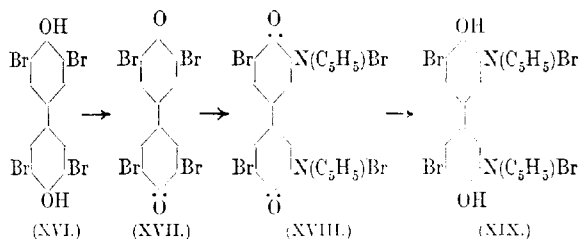
A different reaction takes place if 1:2-naphthaquinone is suspended in pyridine and then treated with one molecular proportion of bromine, as under these conditions the dibromide, which presumably is first formed, loses a molecule of hydrogen bromide and at the same time undergoes pyridinium salt formation, the resulting product being naphthaquinonepyridinium bromide (XIV or XV). The corresponding benzoquinonepyridinium bromide is probably formed when benzoquinone in pyridine solution is treated with bromine, but owing to its excessive solubility we have been unable to isolate it.



On the basis of the mechanism of the formation of pyridinium salts outlined above, quaternary salt formation by the action of pyridine and a halogen should be confined to those phenols which are capable of oxidation to a quinone, that is, to phenols in which there are two hydroxyl groups in the ortho- or para-position to one another. This is in agreement with experiment, as the monohydric phenols and the *m*-dihydric phenols such as resorcinol appear to undergo simple bromination when treated with bromine in pyridine solution. If the replacement of a hydrogen atom in an aromatic compound by a halogen atom is preceded by an additive reaction, then, since in the additive compound the halogen atom must be "aliphatic" in character, there is a possibility of pyridinium salt formation taking place. Such a reaction, however, would have to compete with the tendency of the additive compound to lose hydrogen bromide, a tendency which is always great and which would be enhanced by the presence of the base. Consequently pyridinium salt formation is unlikely to take place, except possibly to a very small extent. Preliminary experiments which we have carried out with certain aromatic hydrocarbons support this view, but in the case of mesitylene and naphthalene we have obtained distinct evidence of the formation of quaternary salts. Up to the present, however, it has not been possible to obtain these in the pure state and therefore we postpone further discussion of this reaction until our work is more advanced.

Since heteronuclear quinones can be obtained from dihydroxy-

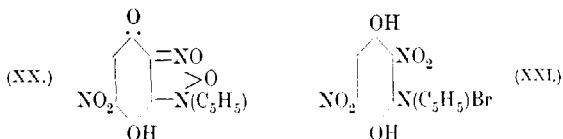
diphenyl derivatives in which the two hydroxyl groups occupy the two para-positions with reference to the point of union of the two rings, it seemed of interest to ascertain if such phenols were capable of undergoing direct quaternary salt formation. We therefore submitted diphenol (*pp'*-dihydroxydiphenyl) to the combined action of bromine and pyridine. As was to be expected, the first action was one of bromination, and pyridinium salt formation only took place when five molecular proportions of bromine were employed. Under these conditions a dark green product was formed which we have been unable to obtain pure, but which on treatment with hydrobromic acid and alcohol underwent reduction to a pale yellow compound which analysis showed to be dibromodiphenyldipyridinium dibromide (XIX). Since the action of four molecules of bromine on diphenol in pyridine solution leads almost exclusively to tetrabromodiphenol (XVI), this tetrabromo-compound must be regarded as being an intermediate product in the formation of the pyridinium salt. The action of the fifth molecule of bromine must, then, be to oxidise this to tetrabromodiphenoquinone (XVII), subsequent pyridinium salt formation taking place between one molecule of this and two molecules of pyridine.



That the halogen atoms in the halogenated quinones are sufficiently reactive to undergo pyridinium salt formation has been shown by Ullmann and Ettisch (*Ber.*, 1921, **54**, [B], 261) in the case of dichloronaphthaquinone, and there can be no reasonable doubt but that the products obtained from chloroanil and pyridine are really pyridinium salts, although not so described by Imbert (*Compt. rend.*, 1901, **133**, 162; *Bull. Soc. chim.*, 1898, [iii], **19**, 1008. Compare also Barnett and Cook, *T.*, 1922, **121**, 1381). The green product referred to above may be dibromodiphenoquinonedipyridinium dibromide (XVIII), but its colour is more in accord with its being of quinhydrone nature.

It has previously been shown by two of us (Barnett and Cook, *loc. cit.*) that the pyridinium salts derived from the hydroxy-

anthraquinones pass easily into phenobetaines. In the case of the pyridinium salts derived from the dihydric phenols of the benzene and naphthalene series this tendency is less marked, although phenobetaines can usually be obtained by the action of ammonia. This increased difficulty in phenobetaine formation is probably to be attributed to the less acidic nature of the phenolic group in the benzene and naphthalene compounds as compared with similar compounds in which the hydroxyl group is directly attached to the anthraquinone ring system. If this is the case, any group which increases the acidic nature of the phenolic hydroxyl group should also increase the tendency to form a phenobetaine. In order to test this point we submitted monobromoquinol and 2:5-dibromoquinol to the simultaneous action of bromine and pyridine. Owing to the uninviting physical properties of the resulting compounds we were unable to obtain them in a state of purity, but the crude substances certainly behaved more like betaines than salts. Greater success was achieved in the case of 2:5-dinitroquinol, as the product obtained in this case was completely free from bromine and was probably the nitrolbetaine (XX). It was easily converted into the bromide (XXI) by recrystallisation from dilute hydrobromic acid, and in this way differs from the nitrolbetaines obtained from 3- and 4-nitroalizarin, as both these separate from hydrobromic acid completely free from bromine.



All the pyridinium salts which we have studied give more or less intense colours on treatment with alkali hydroxides. To some extent the production of these colours is no doubt due to betaine formation, but at the same time it is probable that opening of the pyridine ring takes place with the formation of a derivative of glutaconaldehyde (Zincke, *Annalen*, 1904, **330**, 361; **333**, 296; 1905, **338**, 107; **341**, 365; Zincke and Krollpfeiffer, *ibid.*, 1914, **408**, 285; Zincke and Weisspfenning, *J. pr. Chem.*, 1910, [ii], **82**, 1; 1912, [iii], **85**, 207). Owing to their instability, we have not examined these coloured substances.

EXPERIMENTAL.

Pyridinium Salts Derived from Quinol.

(a) *Quinolpyridinium Bromide* (V).—To a solution of quinol (5.5 grams) in 10 c.c. of pyridine, cooled in a freezing mixture,

bromine (2.5 c.c.; 1 mol.) in 15 c.c. of pyridine was slowly added, and the whole treated after an hour with excess of hydrobromic acid. The resulting bromide, recrystallised from dilute hydrobromic acid, formed slender, yellow needles, m. p. 234–235° (Ortoleva and di Stefano, *loc. cit.*, give m. p. 230°) (Found: Br = 28.1; H₂O = 6.35. C₁₁H₁₀O₂NBr.H₂O requires Br = 28.0; H₂O = 6.29 per cent.). It is not converted into a betaine by alcoholic pyridine. The solutions give a deep red coloration when treated with ammonia, but a betaine could not be isolated. The *picrate* was obtained by adding aqueous picric acid to a solution of the bromide. It crystallised from boiling water, in which it is moderately soluble, in large, orange-yellow needles which melted at 197–199° (Found: N = 12.95. C₁₇H₁₂O₉N₁.H₂O requires N = 12.90 per cent.).

A *perbromide* was obtained by adding bromine water to an aqueous solution of the bromide. It was too unstable to be recrystallised and therefore, after thorough washing, it was dried in a vacuum desiccator (Found: Br = 53.3. C₁₁H₁₀O₂NBr₃.H₂O requires Br = 53.8 per cent.). When boiled with acetone, this perbromide is reduced to quinolpyridinium bromide (identified by the method of mixed melting points and the preparation of the *picrate*), so that perbromide formation apparently takes place without simultaneous oxidation to the quinone. On the other hand, excess of bromine is essential to the production of the perbromide, as it is not obtained when quinolpyridinium bromide is treated with an aqueous solution of exactly one molecule of bromine. It is possible that the hydrobromic acid produced by reducing the perbromide group with acetone reduces the quinone group. Owing to the impossibility of purifying the compound it could not be further examined.

(b) 1:4-Diacetoxypyridinium iodide. — Quinolpyridinium iodide was prepared by Ortoleva and di Stefano's method and after recrystallisation from water was dried at 100°. Five grams of the anhydrous salt, 25 c.c. of pyridine, and 10 c.c. of acetic anhydride were heated together on the water-bath for an hour. After cooling, the crystalline precipitate was collected, washed with a little pyridine, and recrystallised from boiling acetic anhydride. After drying in a vacuum desiccator for several days over concentrated sulphuric acid and solid potassium hydroxide, the product was analysed, the acetyl groups being estimated by distillation with benzenesulphonic acid (Found: I = 31.5; CH₃CO = 22.7. C₁₅H₁₄O₄NI requires I = 31.8; CH₃CO = 21.5 per cent.). This iodide forms small, yellow crystals which darken at 160° and melt to a red liquid at 177–183°. It is very soluble, even in cold water.

(c) *Quinolpyridinium Nitrate*.—The directions given by Ortoleva (*Gazzetta*, 1903, **33**, i, 184) for preparing this compound by adding dilute nitric acid to a suspension of benzoquinone in pyridine invariably lead to resinous products, but it was easily obtained by adding 20 grams of pyridine nitrate, suspended in 40 c.c. of pyridine, to 11 grams of benzoquinone in 25 c.c. of pyridine. Considerable heat was evolved. After heating on the water-bath for thirty minutes, the solution was cooled and the pink precipitate collected, washed with pyridine, and recrystallised twice from water, when it melted at 214–216° and agreed with the description of the nitrate given by Ortoleva. Its picrate was prepared and identified as quinolpyridinium picrate by the method of mixed melting points.

(d) *Quinolpyridinium Sulphate*.—Benzoquinone (5.5 grams) was added to a cold solution of 3 c.c. of concentrated sulphuric acid in 30 c.c. of pyridine, and the whole heated on the water-bath for an hour. The resulting sulphate, after recrystallisation first from aqueous alcohol and then from water, formed yellow plates easily soluble in water but only sparingly soluble in alcohol (Found: S = 6.00, 6.05. $C_{22}H_{20}O_8N_2S_2 \cdot 2H_2O$ requires S = 6.30 per cent.). The water of crystallisation is very firmly held and is not completely lost at 145°. When an aqueous solution of the sulphate is treated with hydrobromic acid, the less soluble bromide, identified by the method of mixed melting points, is precipitated.

(e) *2-Bromoquinol-3-pyridinium Bromide*.—A solution of benzoquinone (5.5 grams) in 50 c.c. of chloroform was cooled in a freezing mixture and treated slowly with 2.5 c.c. (1 mol.) of bromine. After keeping in the freezing mixture for an hour, the whole of the bromine had been taken up with the formation of the quinone dibromide. Pyridine (6 c.c.) was then added, and after keeping for a short time in the freezing mixture the whole was allowed to come to the ordinary temperature and the precipitate washed with chloroform and ether. After repeated recrystallisation from dilute hydrobromic acid this bromide formed straw-coloured needles which were easily soluble in water and alcohol and melted and decomposed at 270–272°. Its solutions give a red coloration on the addition of ammonia or alkali hydroxide (Found: Br = 45.5. $C_{11}H_9O_2NBr_2$ requires Br = 46.1 per cent.). The low value found for bromine was probably due to the presence of a little quinolpyridinium bromide.

Dinitroquinolpyridinium Salts.

(a) *2:5-Dinitroquinolpyridinium Bromide (XXI)*.—Bromine (2.7 c.c.) in pyridine (15 c.c.) was slowly added to 2:5-dinitroquinol

(9.5 grams), suspended in 40 c.c. of pyridine, the whole being cooled in a freezing mixture. A violent reaction took place. After keeping in the freezing mixture for two hours and then over-night at the ordinary temperature, the solid was recrystallised several times from dilute hydrobromic acid and then washed with pyridine. This bromide formed large, yellowish-brown needles which are insoluble in alcohol, ether, and most organic media, and only sparingly soluble in hydrobromic acid. It is converted into the betaine by water, and when heated decomposes without melting (Found: N = 11.5; Br = 22.2. $C_{11}H_8O_6N_3Br$ requires N = 11.7; Br = 22.3 per cent.).

(b) 2:5-Dinitroquinolpyridinium Chloride.—A mixture of 20 grams of dinitroquinol, dissolved in 150 c.c. of alcohol, and 25 c.c. of pyridine* was treated in the cold with 25 grams of finely powdered iodine, and after keeping at the ordinary temperature for two days was heated on the water-bath for one and a half hours. The dark-coloured precipitate was well washed with alcohol and recrystallised from dilute hydrochloric acid. After boiling with acetone, it was again recrystallised from hydrochloric acid and then formed long, bright yellow needles which commenced to decompose at about 180° and melted with profound decomposition at 205° (Found: Cl = 11.6. $C_{11}H_8O_6N_3Cl$ requires Cl = 11.3 per cent.).

(c) Dinitroquinolpyridinium Nitrobetaine (XX).—Three grams of dinitroquinolpyridinium bromide were twice boiled with 500 c.c. of water, and the dark-coloured solid was extracted with alcohol containing a little pyridine. Owing to its insolubility, the betaine could not be recrystallised and therefore was analysed after thorough washing with alcohol and ether. It contained no bromine (Found: N = 14.5. $C_{11}H_7O_6N_3$ requires N = 15.1 per cent.). This betaine does not melt and is somewhat explosive. It is insoluble in all media, but dissolves in dilute acids to form salts. The bromide prepared in this way was identified as dinitroquinolpyridinium bromide by analysis and by direct comparison with a sample prepared in a different way (Found: Br = 22.3. Calc., Br = 22.3 per cent.). It is also soluble in ammonia and the alkali hydroxides, the solutions being deep purple in colour.

If the betaine (3 grams) is suspended in pyridine (25 c.c.) and the whole heated on the water-bath with acetic anhydride (10 c.c.), a bright orange, crystalline powder is obtained. This was insoluble in all media except a mixture of glacial acetic acid and acetic anhydride and would not crystallise from this solvent. We were therefore unable to purify it, but its colour and an acetyl estim-

* Bright orange-red crystals of a pyridine additive compound at once separated, but were not further examined.

ation, performed on the crude substance, pointed to its being a monoacetate of dinitroquinolpyridinium acetate (Found: $C_2H_3O = 19.5$. $C_{15}H_{13}O_5N_3$ requires $C_2H_3O = 22.7$ per cent.). The same compound appears to be formed when the chloride is heated on the water-bath with pyridine and acetic anhydride, but in this case it is exceedingly difficult to obtain a product which is completely free from chlorine (Found: $C_2H_3O = 23.1$ per cent.). The compound slowly develops a purple colour when its aqueous suspensions are treated with ammonia.

An attempt was also made to prepare the acetate by boiling the chloride with acetic anhydride. This was not successful, as decomposition with evolution of nitrogen peroxide took place.

Pyridinium Salts Derived from Catechol.

(a) *Catecholpyridinium Bromide* (VII or VIII).—Bromine (2.5 c.c.; 1 mol.) in pyridine (15 c.c.) was slowly added to catechol (5.5 grams) in 10 c.c. of pyridine, the whole being cooled in a freezing mixture. Absolute alcohol (20 c.c.) was then added and the solid collected after the whole had been kept in a freezing mixture for half an hour. After washing with alcohol, it was recrystallised from dilute hydrobromic acid and then formed long, colourless needles which melted at $267-268^\circ$ (Found: $Br = 29.7$. $C_{11}H_{10}O_2NBr$ requires $Br = 29.8$ per cent.).

The *picrate* was obtained by adding aqueous picric acid to a solution of the bromide. After recrystallisation from boiling water, it formed silky, lemon-yellow needles which melted at $202-203^\circ$ (Found: $N = 13.3$. $C_{17}H_{12}O_5N_4$ requires $N = 13.4$ per cent.).

(b) *1:2-Diacetoxyphenylpyridinium Iodide*.—Catecholpyridinium iodide (2.5 grams), prepared by Ortoleva's method, was heated on the water-bath with 10 c.c. of pyridine and 5 c.c. of acetic anhydride. The iodide first dissolved and then crystals began to separate. After heating for an hour, the whole was cooled and the precipitate recrystallised from acetic anhydride. The purified product was dried for several days in a vacuum desiccator over concentrated sulphuric acid and solid potassium hydroxide and then formed pale yellow leaflets sintering at 190° and melting to a red liquid at $201-204^\circ$ (Found: $I = 31.6$; $C_2H_3O = 21.4$. $C_{15}H_{14}O_4NI$ requires $I = 31.8$; $C_2H_3O = 21.5$ per cent.).

(c) *Catecholpyridinium Betaine*.—Catecholpyridinium bromide, dissolved in hot water, was treated with ammonia. On cooling the dark-coloured solution, yellow needles separated which were free from bromine. After recrystallisation from water, this betaine formed silky, orange needles which decompose without melting

at about 130–140° (Found: C = 59.0; H = 6.15; N = 6.7. $C_{11}H_9O_2N \cdot 2H_2O$ requires C = 59.2; H = 5.83; N = 6.3 per cent.). On drying in a vacuum desiccator, the colour changes to dark red, but reverts to orange almost immediately on exposure to the atmosphere. The aqueous solutions are red and become darker on addition of an alkali.

Pyridinium Salts Derived from 1:2- and 1:4-Naphthaquinone.

(a) *1:2-Naphthaquinone-3(or 4)-pyridinium Bromide* (XIV or XV).—Bromine (5 c.c.) was slowly added to a solution of 16 grams of 1:2-naphthaquinone in 100 c.c. of pyridine, the whole being cooled in a freezing mixture. After keeping over-night at the ordinary temperature, the resulting solution was again cooled in a freezing mixture and the solid washed with pyridine and ether. After being recrystallised four times from a mixture of methyl alcohol and ether, this bromide formed small, orange-brown needles sintering at 195° and melting and decomposing at 201° (Found: Br = 23.8. $C_{15}H_{10}O_2NBr \cdot H_2O$ requires Br = 23.9 per cent.). It is very soluble in water and easily soluble in methyl or ethyl alcohol. Its solutions liberate iodine from hydriodic acid and give an intense purple colour when treated with an alkali hydroxide. On acidifying these purple solutions, the colour is discharged and a red, gelatinous precipitate formed. It is easily reduced by sulphurous acid and then apparently forms a dihydroxynaphthalenepyridinium salt, but the reduction is very difficult to control.

(b) *3(or 4)-Bromo-1:2-naphthaquinone-4(or 3)-pyridinium Bromide* (XI or XIII).—Bromine (5 c.c.; 2 mols.) was slowly added to a solution of 8 grams of 1:2-naphthaquinone in 100 c.c. of chloroform. After keeping for half an hour, 8 c.c. of pyridine were added and the whole was kept for a further period of two hours. The solid was washed with chloroform and ether and then boiled under reflux with acetone in order to destroy any perbromide present. The crude product thus obtained was recrystallised first from dilute hydrobromic acid, then from a mixture of alcohol and ether, and finally from absolute alcohol (Found: C = 46.4, 46.5; H = 3.50, 3.38; Br = 36.3. $C_{15}H_9O_2NBr_2 \cdot C_2H_6O$ requires C = 46.3; H = 3.40; Br = 36.3 per cent.).

If purified by recrystallisation from dilute hydrobromic acid instead of from alcohol, it separates as an orange, crystalline powder which becomes dark red on drying in a vacuum desiccator, but reverts to its former orange colour on exposure to the atmosphere (Found: Br = 40.1. $C_{15}H_9O_2NBr_2$ requires Br = 40.5 per cent.).

This bromide forms orange needles which are easily soluble in water. On heating, it sinters at 241° and melts and decomposes

at 244°. The aqueous solutions give a purple coloration on the addition of an alkali hydroxide, and on acidifying the purple solution a purple precipitate is formed. It liberates iodine from hydriodic acid and is reduced by sulphurous acid to the dihydroxy-compound. The reduced solution was treated with picric acid and the resulting picrate identified as bromodihydroxynaphthalene-pyridinium picrate by the method of mixed melting points.

(c) 3(or 4)-Bromo-1:2-dihydroxynaphthalene-4(or 3)-pyridinium Bromide (X or XII).—Bromine (2.5 c.c.; 1 mol.) was added to 8 grams of 1:2-naphthaquinone in 100 c.c. of ice-cold chloroform. The formation of the naphthaquinone dibromide seemed to be complete after forty minutes, and 4 c.c. of pyridine were then added slowly to the well-cooled solution. The mixture having been kept for an hour, the resulting bromide was washed with chloroform and after being recrystallised twice from dilute hydrobromic acid and twice from a mixture of alcohol and ether formed yellowish-brown needles, which are sparingly soluble in cold water or alcohol (Found: Br = 40.2. $C_{15}H_{11}O_2NBr_2$ requires Br = 40.3 per cent.). When boiled with water, it decomposes into resinous substances, but the decomposition takes place much less easily on boiling with dilute acids. The aqueous solutions give a reddish-brown coloration when treated with an alkali hydroxide, and this colour is almost completely discharged on acidifying. On heating, the bromide sinters at 210° and melts at 217–220°.

The *picrate* was obtained by adding picric acid to a hot solution of the bromide in dilute hydrobromic acid. It is very sparingly soluble, but can be recrystallised from very dilute hydrochloric acid, and then forms a lemon-yellow, crystalline powder which melts at 197–200° (Found: N = 10.1. $C_{21}H_{13}O_9N_4Br$ requires N = 10.3 per cent.).

(d) 1:4-Dihydroxynaphthalene-3-pyridinium Bromide (VI).—Three grams of 1:4-naphthaquinone, 5 grams of pyridine hydrobromide, and 10 c.c. of pyridine were heated together on the water-bath for three and a half hours. The dark-coloured precipitate, having been washed with absolute alcohol to remove resinous matter, was recrystallised from a mixture of methyl alcohol and ether and finally from dilute hydrobromic acid. This bromide forms long, brown needles which melt and decompose at 214–216° (Found: Br = 24.0. $C_{15}H_{11}O_2NBr \cdot H_2O$ requires Br = 23.8 per cent.). It is sparingly soluble in cold water or cold alcohol, the aqueous solution developing a deep purple coloration on the addition of an alkali hydroxide.

Experiments were also made with a view to obtain pyridinium compounds by the action of bromine on a solution of 1:4-naphtha-

quinone in pyridine, and by the action of pyridine on a chloroform solution of 1:4-naphthaquinone dibromide. In both cases, products were obtained which contained bromine and nitrogen, but owing to their insolubility it was not found possible to purify them. They were probably betaines, for they became much paler in colour on treatment with acids, but as they remained insoluble it seems likely that they were of complex nature.

Action of Pyridine and Bromine on 4:4'-Dihydroxydiphenyl.

(a) *Tetrabromodiphenol*.—Bromine (2.1 c.c.; 4 mols.) was slowly added to a well-cooled solution of 2 grams of diphenol in 15 c.c. of pyridine. After keeping over-night, the greenish-black solid was washed with pyridine and ether and then boiled with alcohol containing hydrobromic acid. This treatment discharged the colour, and almost colourless crystals were obtained from the solution by diluting with water and then cooling. These were identified as tetrabromodiphenol by the method of mixed melting points.

(b) *3:3'-Dibromo-4:4'-dihydroxydiphenyl-5:5'-dipyridinium Dibromide (XIX)*.—Two grams of diphenol in 15 c.c. of pyridine were treated as described above with 2.5 c.c. of bromine (5 mols.) in 25 c.c. of pyridine. The green product, on boiling with alcohol containing hydrobromic acid, dissolved to an almost colourless solution, and at the same time a penetrating smell of brominated alcohol derivatives was produced. A sample of the alcoholic solution gave no tetrabromodiphenol on dilution with water. On cooling, an orange-yellow substance crystallised out. This was recrystallised first from hydrobromic acid, then from absolute alcohol, and finally again from hydrobromic acid, and then formed straw-coloured needles which melt and decompose at 325° (Found: N = 4.11; Br = 48.1. $C_{22}H_{16}O_2N_2Br_4$ requires N = 4.24; Br = 48.5 per cent.). It is very sparingly soluble in cold water or cold alcohol, more readily soluble when hot. The aqueous solutions become bright orange-red on the addition of ammonia or an alkali hydroxide.

Summary.

1. It has been shown that the products obtained from quinol and catechol by treating them with pyridine and a halogen, and by the action of pyridine salts on *p*-benzoquinone, are dihydroxy-phenylpyridinium salts.
2. The formation of phenobetaines from these compounds and from similar salts from dinitroquinol has been studied.
3. The reaction has been extended to the naphthalene series

and in the case of 1:2-naphthaquinone both the bromodihydroxy-naphthalenepyridinium bromide and the corresponding bromo-naphthaquinonepyridinium bromide have been isolated.

4. It has been shown that diphenol is also capable of direct pyridinium salt formation by treatment with bromine in the presence of pyridine.

In conclusion, the authors desire to express their thanks to the South Metropolitan Gas Co. for gifts of pyridine, and to the Research Fund Committee of the Chemical Society for a grant which has defrayed some of the expenses of this research.

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[Received, December 29th, 1922.]

LXIV.—*The Constitution of Polysaccharides. Part VI. The Molecular Structure of Cotton Cellulose.**

By JAMES COLQUHOUN IRVINE and EDMUND LANGLEY HIRST.

It will be generally admitted that a complete study of cellulose must include, in addition to purely chemical inquiries, physical investigations on the mechanism whereby discrete particles are arranged to form organised structures possessing the properties of fibres. Nevertheless there are good reasons for claiming that cellulose is based on a molecular unit, although most chemists will agree that the identification of this unit represents the solution of only one of a series of complicated problems.

Constitutional studies of this type are beset with unusual experimental difficulties and speculation is hazardous, but many of the investigators who have been attracted to this field have proposed structural formulæ with a confidence which the experimental evidence and the present state of knowledge regarding the simple sugars do not justify. As a result, the extensive literature on the constitution of cellulose contains many conflicting statements and suggestions which make for confusion rather than enlightenment. Accordingly it is not proposed at this stage to review in detail the earlier publications on the subject.

A series of investigations on the molecular constitution of cellu-

* As the title of this communication implies, the results now submitted were obtained with cotton cellulose. It has thus been considered unnecessary to specify throughout the text the particular form of the polysaccharide to which the paper refers.

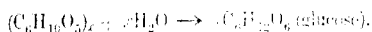
lose was commenced in this laboratory twelve years ago, the work being based on the idea that the structure of compounds related to the sugars may be solved by the methylation method devised by one of us. The main inquiry was supplemented by cognate researches designed to provide the methylated sugars which would serve as the reference compounds necessary for the interpretation of the results. The information obtained in the course of these related researches is focussed in the evidence now submitted, and leads to a constitutional formula which expresses the molecular unit of cellulose in the simplest possible terms.

Two well-established reactions form the basis of the argument :

(1) cellulose $(C_6H_{10}O_5)_n$, on complete hydrolysis, is converted quantitatively into glucose,

(2) the graded hydrolysis undergone by cellulose during "aceto-lysis" may be arrested at a stage where the disaccharide cellobiose is a definite product.

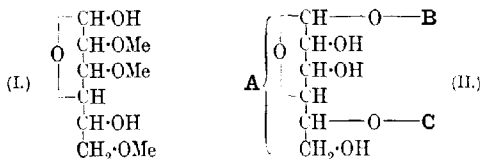
The first of these considerations has been upheld for many years, but the evidence generally put forward in support of the view that cellulose is composed entirely of glucose residues does not carry conviction to workers in the sugar group. We have, however, shown recently (Irvine and Soutar, T., 1920, 227, 1489; Irvine and Hirst, T., 1922, 124, 1585) that the transformation of cellulose into pure crystalline methylglucoside can be effected in yields which are at least 95 per cent. of the theoretical amount, and may be regarded as quantitative. This result has been confirmed by an independent method (Moller-Wilms, T., 1921, 219, 803) and it may be concluded that the ultimate hydrolysis of cellulose proceeds according to the equation



Intermediate steps in the above reaction are unknown beyond the fact that, under special conditions, cellobiose is a penultimate product. It is evident, therefore, that hydrolysis gives no clue to the molecular magnitude of the cellulose unit or to the inner constitution. The hydroxyl groups involved in the union of the glucose residues and the nature of the internal oxygen ring or rings present in each hexose component are likewise unknown. These factors, the absence of which accounts for much confusion in cellulose formulae, have now been supplied by substituting methoxyl groups for all the hydroxyl groups in cellobiose and thereafter subjecting the alkylated polysaccharide to hydrolysis.

The methylation of cellulose was first undertaken by Denham and Woodhouse (T., 1913, 103, 1735 and subsequent papers), and as the solubilities prohibited the use of the silver oxide reaction,

the alkylation was effected by means of methyl sulphate and sodium hydroxide. Although alkylation proved to be difficult, the reaction proceeded normally and ultimately a methylated cellulose containing 25 per cent. of methoxyl was produced. The alkyloxy groups survived the action of all ordinary reagents including the highly concentrated hydrochloric acid which was used to hydrolyse the compound. One of the products then obtained was a crystalline trimethyl glucose, and the result has a double importance in being the first preparation of a methylated sugar by the methyl sulphate reaction and in furnishing a sugar which, next to crystalline tetramethyl glucose, is the most important reference compound so far known in this type of inquiry. The study of this particular trimethyl glucose was immediately undertaken and, in the course of a laborious research, Denham and Woodhouse (T., 1917, 111, 244) obtained experimental evidence pointing to the structure shown in Formula I. This constitution was subsequently supported by Haworth and Leitch (T., 1918, 113, 188) and confirmed by Irvine and Hirst (T., 1922, 121, 1213).



The formation of 2:3:6-trimethyl glucose from cellulose shows that positions 1 and 5 of a glucose residue must have been protected from methylation. It follows, therefore, that cellulose is a derivative of glucose in which positions 1 and 5 are substituted by one or more anhydro-glucose residues. Beyond this, the experimental evidence hitherto available does not go, and the limitation is expressed in Formula II, which represents the molecular unit of the polysaccharide as composed of three sections, A, B, and C. As some misconception seems to have arisen on this point, it is necessary to recall that the methylated cellulose employed by Denham when he discovered trimethyl glucose contained only 25 per cent. of methoxyl, a value which is considerably lower than that required for a dimethyl derivative (32.6 per cent.). As a necessary consequence, the product of hydrolysis was a complex mixture, of which 2:3:6-trimethyl glucose was only one of many components. Of the three sections, A, B, and C, into which the cellulose molecule has now been mapped, A alone has been fully explored. The only claim which could be made regarding B and C was that they must consist of anhydro-glucose residues. B and C

might be constituted in any manner or be related to any of the isomeric forms of glucose. They might be uniform with each other and with A, or all might be different. Obviously, a decisive answer to the issues thus raised could be obtained only by carrying out the methylation of cellulose to the maximum extent, and by identifying *each* of the methylated sugars thereafter formed on hydrolysis.

Researches were undertaken to complete the work on these lines, but the war intervened, so that the evidence required to formulate sections B and C of the cellulose molecule is available now for the first time. Meanwhile, however, others have not refrained from utilising the incomplete results or from propounding formulæ for cellulose based directly on Denham's earlier work. This will be referred to later.

At the request of, and in consultation with, Dr. Denham, we have repeated and extended his experiments, and find that the progressive methylation of cotton cellulose is facilitated, not so much by the use of large excesses of the methylating agents as by frequent repetition of the treatments with the alkylating mixture. As described in the experimental part, when the process of methylation followed by isolation of the product is repeated fourteen times, the methoxyl content increases to the observed maximum of 43.8 per cent. This is slightly less than the highest value found by Denham (44.6 per cent., T., 1921, 119, 77) and is in satisfactory agreement with the value required for a trimethyl cellulose ($\text{OMe} = 45.5$ per cent.). No further increase in the methoxyl content was obtained on continuing the methylation twenty times. It is thus clear that the experimental procedure did not involve oxidation or the hydrolytic cleavage of the polysaccharide, and the result confirms the view that on an average there are three hydroxyl groups for every six carbon atoms present in the molecule.

Trimethyl cellulose is a white solid which retains the microscopic appearance of the original cotton and is remarkably insoluble in organic solvents. The physical condition of the compound varies greatly according to the method of drying, the substance becoming horny and semi-vitreous when heated in the moist condition at 100° . When dehydration is effected by successive immersion in alcohol and ether, followed by prolonged drying in a vacuum oven at a low temperature, the compound can be disintegrated to a white solid resembling starch in appearance.

On previous occasions, the hydrolysis of the partly methylated celluloses then available was carried out by the agency of highly concentrated hydrochloric acid, but the method was inapplicable in the present instance, as quantitative results were desired.

Resource was therefore had to heating with methyl alcohol containing hydrogen chloride—a process which effects hydrolysis and condensation of the products with the solvent. In the examination of the methylated glucosides thus produced, a number of considerations had to be kept in view. It will be evident that in the event of the fragments of the cellulose molecule indexed as A, B, and C proving to be identical, a trimethyl cellulose could yield no sugar other than 2:3:6-trimethyl glucose. But although B and C may resemble A in being derived from the butylene-oxide form of glucose, they may differ in the position of the hydroxyl groups through which they are mutually linked. In such a case, a mixture of *isomeric* trimethyl glucoses would be formed. The number of isomeric sugars would be further increased if the fragments B and C belong to the γ -series,* and the final possibility remains that the distribution of the hydroxyl groups between the sugar residues in cellulose may not be uniform. In other words, the frequently-quoted statement that cellulose contains three hydroxyl groups per C_6 unit has a limited significance and may involve nothing more than that this is an average value, some glucose residues having more than three such groups, and others less. Taking all these possibilities into account, the hydrolysis of trimethyl cellulose might proceed in any one of the four ways indicated below:

		No. of possible forms, including γ -isomerides.
Trimethyl cellulose	One variety of trimethyl glucose	1
	A mixture of isomeric trimethyl glucoses of the butylene-oxide type	4
	A mixture of isomeric trimethyl glucoses including γ -forms	20
	Tetramethyl glucose x mols.	5
	Trimethyl glucoses y mols.	20
	Dimethyl glucose z mols.	24

Excluding α - and β -isomerides, the largest number of possible sugars which might be encountered is forty-nine and the experimental treatment was designed to separate these products if present. Contrary to expectation, the result actually obtained was the simplest of all the possibilities discussed. In the reaction now under consideration (which yields the methylglucosides corresponding to the hydrolysis sugars), the product was identified as the equilibrium mixture of α - and β -2:3:6-trimethyl methyl-

* The expression γ -series is used here to designate all forms of glucose in which the internal oxygen ring is not of the butylene-oxide type.

glucosides. When hydrolysed in the usual manner, the glucoside gave crystalline trimethyl glucose alone. *The main product was uniform. No isomerides were present: tetramethyl glucose, monomethyl glucose, glucose, and γ -sugars were definitely absent.* As was to be expected, a small quantity of dimethyl methylglucoside was isolated from residues, but the amount of this impurity corresponded exactly with the margin of deficiency (2.6 per cent.) in the methoxyl content of the methylated cellulose used. The result is important and simplifies enormously the problem of the molecular structure of cellulose, particularly when the yields obtained at the different stages are taken into account.

Stage I. Methylation of cellulose to dimethyl cellulose, 91 per cent.

Stage II. Methylation of dimethyl cellulose to trimethyl cellulose, 77 per cent.

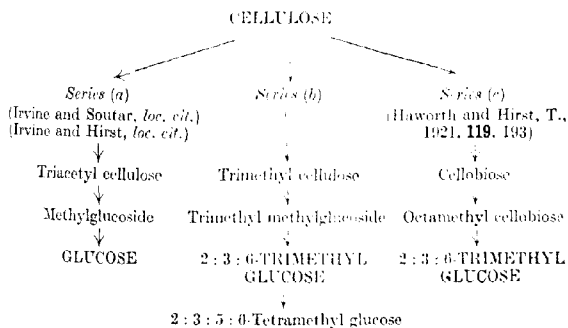
Stage III. Conversion of trimethyl cellulose into trimethyl methylglucoside (distilled), 91.5 per cent.

Stage IV. Conversion of trimethyl methylglucoside into 2 : 3 : 6-trimethyl glucose (crystalline), 86 per cent.

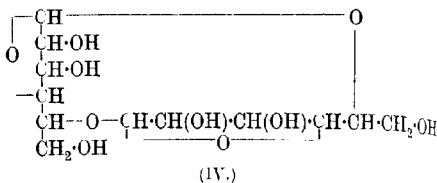
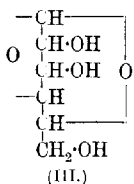
In the above table, the yields are quoted in percentages of the theoretical amount and refer to analytically pure products. Stages I and II involved inevitable mechanical losses during the frequent methylations. It may be mentioned, however, that the yields from stages III and IV were actually quantitative when based on polarimetric evidence and were much superior to those obtained in the standard preparations of the same compounds.

Discussion of Results.

To facilitate description, a synopsis of the reactions of primary importance in arriving at the molecular unit of cellulose is given below:



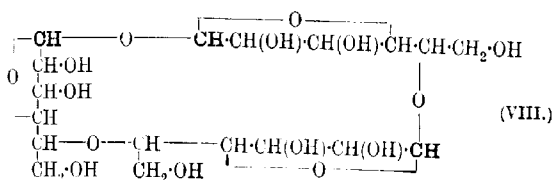
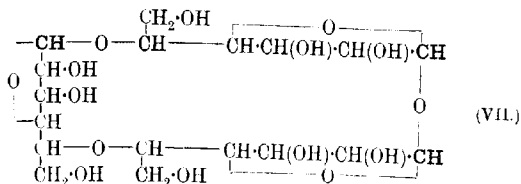
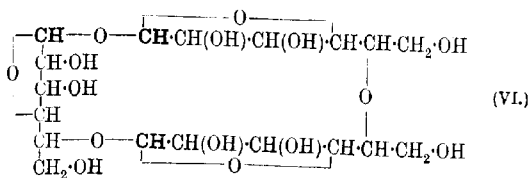
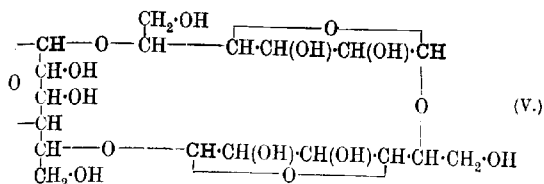
The simplest molecule which will satisfy the conditions of series (a) and (b) is that of a 1:5-anhydroglucose of the butylene-oxide type (Formula III).



Such a structure would, however, be incapable of yielding cellobiose and of conforming to the requirements of series (c), unless it is assumed that the disaccharide is an adventitious product formed during acetolysis by the autocondensation of glucose. Experimental evidence is entirely opposed to this view and, further, octa-acetyl cellobiose has never been prepared from penta-acetyl glucose. Moreover, the linkage of the two glucose residues in cellobiose is characteristic only of natural carbohydrates and has been detected in lactose (Haworth and Leitch, T., 1918, 113, 188), in starch (Irvine and Macdonald, *Brit. Assoc. Reports*, 1922; *J. Soc. Chem. Ind.*, 1922, 41, 363R), and in glycogen (Macheth and Mackay; unpublished result). These observations lead inevitably to the conclusion that the cellobiose residue is preformed in the cellulose molecule and consequently the unit of the polysaccharide must contain, at least, two glucose residues. In order to conform to the structure of cellobiose, these must be united as in Formula IV.

In terms of this formula, however, 100 parts of cellulose should give 105.5 parts of cellobiose, and although, considering the conditions employed in such reactions, it is not to be expected that the maximum should be realised in practice, the yields of the disaccharide are extremely variable and rarely exceed 35 per cent. The highest recorded are of the order 50–60 per cent., and in the meantime it is prudent to select a formula for cellulose which will give a yield of cellobiose approximating to this figure rather than to the higher value 105.5. On this basis, the simplest formula is that of a tri-anhydroglucose which can be constituted in four ways whilst preserving the necessary 1:5-linkage. These alternatives are expressed in Formulæ V, VI, VII, and VIII.

All the structures satisfy quantitatively the primary conditions of the conversion of cellulose into glucose and into the correct isomeric form of trimethyl glucose. In addition, the maximum theoretical yield of cellobiose would be in each case 70 per cent.



Letters in block type designate the potential reducing groups.

together with 37 per cent. of glucose. The methylation process gives no help in discriminating between the alternatives, and other characteristic chemical reactions of cellulose are accounted for by any of the formulae. It will be seen, however, that compounds possessing the structure of formulae VI, VII, and VIII could give rise to cellobiose in one particular way only and might yield in addition either

(a) a non-reducing glucose glucoside,

or (b) a doubly reducing diglucose of a type which is unknown.*

* Ost and Prosiegel (*Z. anorg. Chem.*, 1920, **33**, 100) describe an isocellobiose obtained by the acetolysis of cellulose. It is doubtful if this is a single chemical individual, but as the reducing power is equal to that of maltose the compound cannot correspond with either of the disaccharides postulated above.

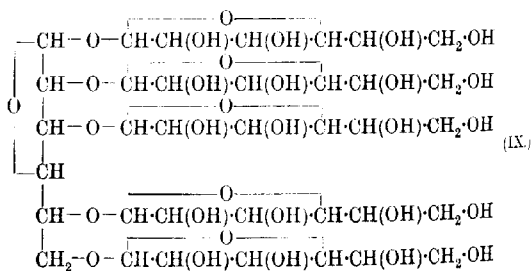
On the other hand, the graded hydrolysis of a compound formulated as in V would result in cellobiose as the only possible disaccharide.

Taking all available factors into account, we prefer Formula V as the simplest expression of a molecule which, polymerised in unknown numbers, would represent cellulose as a chemical entity, but we recognise that any odd number of anhydroglucose residues from three upwards can be arranged so as to fulfil the conditions. Our work gives no indication of the degree of polymerisation undergone by the molecular unit, but the extreme insolubility of trimethyl cellulose compared with the ready solubility of methylated starch, inulin, and glycogen points to the idea that cellulose is the most highly polymerised of the known polysaccharides. This subject is engaging our attention together with the cognate problem of the depolymerisation of cellulose. In addition, other standard forms of cellulose are being examined on the lines indicated in this paper as part of our general programme of research on polysaccharides. We are also engaged with experiments designed to identify disaccharides other than cellobiose among the degradation products of cellulose and reserve the structural study of such compounds.

Discussion of Other Formulæ for Cellulose.

Of the various structures which have been suggested, consideration may be limited to formulæ expressing a relationship between cellulose and glucose. These may be classified approximately under headings.

1. *Formulæ Modelled on that of the Glucosides.*—Hess has proposed a variety of glucosidic structures for cellulose which bear a general resemblance to Fischer's formula for tannins. The simplest example is shown below, variations being introduced by lengthening any of the sugar chains.

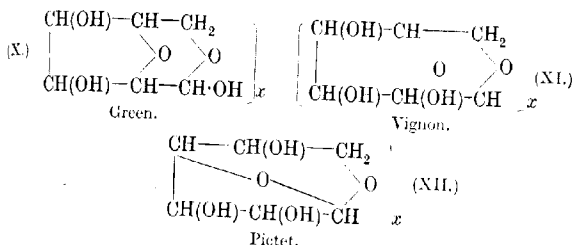


By our processes, the above structure would give five molecules

of 2:3:5:6-tetramethyl glucose and one molecule of glucose, while the same products, together with trimethyl glucose, would be obtained from the more complex formulæ suggested by Hess. Our results are entirely opposed to this view or to any formula in which the hydroxyl groups are not symmetrically distributed.

2. *Formulae Based on Haworth and Hirst's Constitution for Cellobiose.*—Karrer (*Helv. Chim. Acta*, 1921, 5, 187), recognising that the structure of cellobiose must be repeated in cellulose, has claimed on slender experimental grounds that cellulose is a polymeride of a form of anhydrocellobiose for which he has devised the name "cellosan." The formula need not be reproduced. On methylation and hydrolysis, the hypothetical "cellosan" would give equimolecular proportions of 2:3:6- and 2:3:5-trimethyl glucose. No trace of the latter compound was formed from methylated cellulose and Karrer's formula is manifestly incorrect.

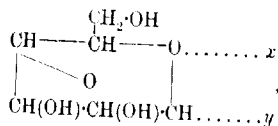
3. *Formulae Based on Anhydroglucoses.*—Three examples may be quoted.



Each of the above structures would give a trimethyl cellulose, but subsequent hydrolysis would yield

- (a) a dimethyl glucose from X,
- (b) 2:3:4-trimethyl glucose from XI,
- (c) 2:3:5-trimethyl glucose from XII.

In no case are these conditions supported by our results. Reference may also be made under this heading to the formula suggested by Hibbert. In a review (*J. Ind. Eng. Chem.*, 1921, 13, 256, 334) of the standard constitutional reactions of cellulose, he proposes the structure



in which polymerisation proceeds by the addition of similar units at x and y . Two such additions, arbitrarily arranged, give

the same structure as Formula V and, presumably this method of addition could be extended indefinitely. As already stated, we do not agree with the view that cellulose is based on a single hexosan unit or on any molecule which contains an even number of such units. Nor is it likely, in view of the results obtained by the polymerisation of glucosan (Irvine and Oldham, *Brit. Assoc. Reports*, 1922), that the mechanism suggested by Hibbert is functional in the formation of the cellulose complex. Hibbert's method of building up the cellulose molecule was based on an assumption which was premature. He assumed that the fractions x and y are identical with each other and with the nucleus unit, whereas the quantitative evidence required to decide this point is now contributed for the first time. Nevertheless Hibbert states in his paper that Denham and Woodhouse had obtained trimethyl glucose "by the hydrolysis of completely methylated cellulose." Of the reasons adduced in favour of his formula, only one (this misquotation of Denham and Woodhouse's result) has any quantitative structural significance. Although one expansion of his formula coincides with that which we show to be consistent with our complete results, reference to the introduction will disclose how many possibilities were overlooked by Hibbert in his speculations.

The constitution of the cellulose molecular unit proposed by us depends on three factors taken in conjunction. These have all been investigated here and are : (1) the proof that one fragment of the molecule consists of 1:5-anhydroglucose (Denham); (2) the proof that the same fragment is present in cellobiose, which is thus an integral part of the cellulose molecule (Haworth and Hirst); and (3) the proof now contributed that *all* the glucose residues in cellulose are identical.

A constitutional formula arrived at in the absence of any one of these factors is logically invalid.

EXPERIMENTAL.

Trimethyl Cellulose.

Trimethyl cellulose was prepared essentially by the method already described (Denham, *T.*, 1921, 119, 77).

Cotton cellulose was in the first instance methylated to the dimethyl stage by the joint action of methyl sulphate and 30 per cent. aqueous sodium hydroxide. After four such treatments the procedure was varied and, in the subsequent alkylations, the methyl sulphate was dissolved in ether and the sodium hydroxide in methyl alcohol. The methoxyl content increased slowly in

the course of each successive alkylation and, after twelve treatments, was between 42 and 43 per cent. As this value was not exceeded, even when the methylation was repeated twenty times, it is apparently the experimental maximum.

Up to the stage where dimethyl cellulose was the essential product, the weight of material obtained averaged 91 per cent. of the theoretical amount, but the introduction of the third methyl group diminished the over-all yield to 70 per cent. This figure, in view of the difficulty experienced in avoiding mechanical losses, must be regarded as considerably short of the maximum. Four independent preparations were carried out, the composition of the different specimens being given below :

Specimen A	12 methylations.	OMe = 42.0 per cent.
" B	17 "	OMe = 43.1 "
" C	14 "	OMe = 43.0 "
" D	14 "	OMe = 43.8 "

A uniform mixture gave OMe = 43.1, whereas trimethyl cellulose, $C_6H_7O_2(OMe)_3$, requires OMe = 45.5 per cent.

It should be stated that Schweitzer's reagent was not used at any stage to remove partly methylated material from the products, which thus retained the essential microscopic structure of the original cellulose. The evidence of hydrolysis submitted later showed that the preparation consisted of trimethyl cellulose (85 per cent.) mixed with dimethyl cellulose (15 per cent.).

Simultaneous Hydrolysis of Trimethyl Cellulose and Condensation of the Product with Methyl Alcohol.

The four specimens of methylated cellulose were uniformly mixed and heated for fifty hours at 100° with excess of methyl alcohol containing 1 per cent. of hydrogen chloride. The most suitable charge for a sealed tube was found to be 4.5 grams of the solid and 60 c.c. of the acid reagent. As the decomposition was incomplete under the conditions stated, the heating was continued for a further period of fifty hours at 130°. Only a minute quantity of a flocculent solid then remained undissolved and the solution had acquired a faint yellow colour. Examination showed that this trace of solid residue consisted mainly of mineral matter and it was accordingly neglected. The solution, which contained the hydrolysis sugar in the form of the corresponding methylglucoside, was neutralised with silver carbonate, filtered, treated with charcoal, and evaporated under diminished pressure. A colourless syrup remained which, after drying at 100°/10 mm. until constant in weight, amounted to 95 per cent. of the theoretical amount calculated.

ing on the conversion of a trimethyl cellulose into trimethyl methylglucoside. The syrup was distilled in a high vacuum, a small first fraction being collected in order to ascertain if any tetramethyl methylglucoside was present.

		B. p.	n_D	OMe.
First fraction	8.6 per cent.	115°/0.6 mm.	1.4591	52.3 per cent.
Main " " " " " "	74.7 " "	115—118°/0.5 mm.	1.4590	52.5 " "
High " " " " " "	11.5 " "	120—130°/0.5 mm.	1.4665	47.0 " "
Residue " " " " " "	5.1 " "	—	—	—

The constants determined on the first fraction agree exactly with those given by 2:3:6-trimethyl methylglucoside and show that tetramethyl methylglucoside was absent. Even a trace of the latter compound would have been detected by an elevation of the methoxyl content and a depression of the refractive index. Fractions I and II were accordingly united as identical, and found to be pure trimethyl methylglucoside [Found: C = 50.72; H = 8.58; OMe = 52.5; n_D 1.4590. $C_6H_8O_2(OMe)_4$ requires C = 50.85; H = 8.47; OMe = 52.6 per cent.; n_D 1.4583].

Nucleation of the liquid glucoside with 2:3:5-trimethyl methylglucoside (prepared from glucosan) failed to induce crystallisation and the compound was further identified as the 2:3:6-isomeride by the determination of the specific rotation.

Solvent.	c.	$[\alpha]_D^{20}$.
Methyl alcohol	1.05	+ 72.0°
Chloroform	1.34	66.0

Analysis of the fraction of higher boiling point and of the syrup remaining undistilled showed that this material was a mixture of 40 per cent. of trimethyl methylglucoside with 60 per cent. of dimethyl methylglucoside. This is in agreement with the idea that the original methylated cellulose contained 85 per cent. of trimethyl cellulose and 15 per cent. of dimethyl cellulose, a result already indicated by analysis (Found: OMe = 43.1. Calc., OMe = 43.6 per cent.). Allowing for this proportion of incompletely methylated material, the yield of pure distilled 2:3:6-trimethyl methylglucoside was 91.5 per cent. of the theoretical amount.

Hydrolysis of Trimethyl Methylglucoside from Trimethyl Cellulose.

In order to confirm the presence of both the α - and β -forms of 2:3:6-trimethyl methylglucoside, the compound was hydrolysed in one experiment under conditions which would display the characteristic rise and fall in rotation. The polarimetric record of the reaction thus obtained agreed exactly with that previously determined by Irvine and Hirst (*loc. cit.*).

Solvent 3.2 per cent. aqueous hydrochloric acid, $c = 2.5$.

Time.	Temperature.	$[\alpha]_D^{20}$.
5 minutes	90°	+ 84.5°
35 "	"	90.0
75 "	"	94.4
6 hours	100	* 76.0
7 "	"	* 72.0

* Value calculated on the weight of sugar formed.

Isolation of the product in the usual manner gave a viscous syrup which, on nucleation, rapidly solidified. The crystals, when purified, were identified as 2:3:6-trimethyl glucose. Yield 50 per cent.

Quantitative Hydrolysis. Yield of Trimethyl Glucose.

In repeating the hydrolysis on a larger scale the procedure was varied to obtain more accurate data as to the weight of sugar formed. A 4 per cent. solution of trimethyl methylglucoside in 5 per cent. aqueous hydrochloric acid was boiled under a reflux condenser until the activity became constant ($[\alpha]_D + 72^\circ$ in three hours). The presence of a small quantity of charcoal prevented the formation of coloured by-products during the hydrolysis.

After neutralisation with barium carbonate, the solution was evaporated under diminished pressure and the residue extracted with dry ether. Removal of the solvent gave a syrup which, when nucleated with 2:3:6-trimethyl glucose, solidified immediately to a hard, crystalline mass. Yield 86 per cent. of the theoretical amount. Without further purification, the sugar melted at 94—104°, and this value was unaffected by admixture with an authentic specimen of crystalline trimethyl glucose [Found: C = 48.50; H = 8.27; OMe = 41.2. $C_6H_8O_3(OMe)_3$ requires C = 48.65; H = 8.11; OMe = 41.9 per cent.]. The purity of the material was further confirmed by determining the specific rotation in methyl alcohol before and after catalysis with a trace of hydrochloric acid. Initial $[\alpha]_D^{20} + 92.5^\circ \rightarrow$ constant $[\alpha]_D^{20} - 66.5^\circ$ for $c = 1.35$.

Proof that Tetramethyl Glucose was Absent.—The finely-powdered sugar was boiled for several hours under a reflux condenser with a large excess of light petroleum. On evaporation of the filtered liquid no trace of residue remained and a similarly negative result was obtained on repeating the extraction. As by this process it is possible to identify with certainty as little as 0.01 gram of tetramethyl glucose, we conclude that this particular sugar was entirely absent.

Proof that only 2:3:6-Trimethyl Glucose was Present.—After drying to remove low-boiling petroleum, the whole of the sugar was recrystallised fractionally from dry ether. This treatment

affected only the melting point, which increased to $104-108^{\circ}$. When mixed with an authentic specimen of 2:3:6-trimethyl glucose melting at $105-109^{\circ}$, the value was unchanged ($104-107^{\circ}$).

Recrystallisation had increased the proportion of the α -form of the sugar present in the mixture, and the initial specific rotation in methyl alcohol had therefore risen to $+108^{\circ}$. This diminished to $+67^{\circ}$ after catalysis and the figures are in excellent agreement with the standard values for 2:3:6-trimethyl glucose. It is important to state that the total ethereal mother-liquors collected during the recrystallisation of the sugar were united and evaporated. The resulting syrup again solidified completely to a mass of crystals, thus proving that no liquid isomeric form of trimethyl glucose was present.

As the conversion of trimethyl cellulose to trimethyl methyl-glucoside was effected in 91.5 per cent. yield, and as the pure sugar thereafter obtained from the glucoside amounted to 86 per cent. of the calculated value, the over-all yield for the series of reactions is 78.7 per cent. as a minimum.

The authors desire to express their indebtedness to The Carnegie Trust for a grant in aid of the work, and to Dr. W. S. Denham for a generous supply of methylated cellulose.

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LXV.—*Researches on Pseudo-Bases. Part IV. A New Synthesis of Tertiary Amines of the Form $R \cdot CH_2 \cdot NR^1R^2$.*

By GERTRUDE MAUD ROBINSON and ROBERT ROBINSON.

ALTHOUGH a variety of methods are available for the synthesis of primary and secondary amines of the aliphatic, alicyclic or fatty-aromatic series, the related tertiary bases must usually be prepared by some process of direct alkylation, and this method, although generally applicable, has certain serious disadvantages in many cases. Often it is difficult to control, the main product being a quaternary ammonium salt, and in other examples the required alkyl halide (or sulphuric ester) is not readily accessible. The experiments now to be described improve the position to the extent that if $R \cdot OH$ is a readily accessible alcohol convertible into an organo-magnesium compound $R \cdot Mg \cdot hal$, it is possible to produce

in a simple operation a base of the formula $R\cdot CH_2\cdot NR^1R^2$. The methylene group is derived from formaldehyde, and experiments are in progress the object of which is to extend the reaction to other aldehydes and so obtain amines typified by the expression $R\cdot CHR^1\cdot NR^2R^3$.

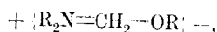
Before dealing with the process itself, it is desirable to make brief reference to the theoretical considerations which it involves and which led us to anticipate that the fundamental reaction would occur.

The constitutional analogy between cotarnine and the simple pseudo-bases of the type $NR_2\cdot CH_2\cdot OH$ suggested that the latter should condense with alcohols so as to form ethers, $NR_2\cdot CH_2\cdot OR$; and in Part III of this investigation (McLeod and G. M. Robinson, T., 1921, 119, 1470) the verification of this prediction was recorded. It was found that the condensation proceeded to a greater extent to completion when the higher alcohols were employed than was the case with ethyl and propyl alcohols and we have now used *n*-butyl alcohol with satisfactory results.

By further reasoning from analogies with cotarnine derivatives, and on account of the ease of hydrolysis of these ethers and their reactivity towards substances such as ethyl cyanoacetate, it seems fair to conclude that the formulation given above is an inadequate representation of their chemical behaviour, which is in accord with the existence of the equilibrium

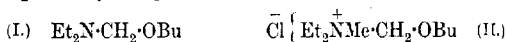


But since these substances may be distilled without decomposition, the existence of any actual ammonium alkyl oxide seems unlikely and the constitution of the members of this group is, we think, best represented by the formula



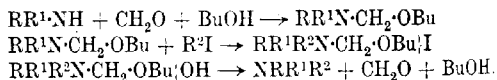
which symbolises a partial intramolecular electrovalency connecting the nitrogen and oxygen atoms. Thus the easy hydrolysis and high reactivity are clearly connected with the "onium" tendencies of the nitrogen atom and this conception affords a ready explanation of the otherwise curious fact that the acetals, $RO\cdot CH_2\cdot OR$, are so much less reactive than the amino-ethers, $R_2N\cdot CH_2\cdot OR$. The condition which facilitates the hydrolytic fission of a molecule $-ab-$ into $-aH$ and $HOb-$ is that *a* should be electronegative and *b* electropositive either because of their inherent character or as the result of an induced alternate polarity effect. The following example will suffice to illustrate this

point. In the series $\text{CH}_3\cdot\text{CH}_2\cdot\overset{+}{\text{O}}\text{CH}_2\cdot\text{CH}_3$, $\text{CH}_3\cdot\text{CH}_2\cdot\overset{+}{\text{O}}\text{CH}(\text{OEt})\cdot\text{CH}_3$, $\text{CH}_3\cdot\text{CH}_2\cdot\overset{+}{\text{O}}\text{CO}\cdot\text{CH}_3$, $\text{CH}_3\cdot\overset{+}{\text{CO}}\cdot\overset{+}{\text{O}}\text{CO}\cdot\text{CH}_3$, $\text{Cl}\cdot\overset{+}{\text{CO}}\cdot\text{CH}_3$, $\text{Cl}\cdot\overset{+}{\text{CH}_2}\cdot\overset{+}{\text{O}}\cdot\text{CH}_3$, $\text{Cl}\cdot\text{CH}_2\cdot\text{CH}_3$, the ease of hydrolysis rises to a maximum at acetyl chloride, where the polarity differentiation is greatest, and then falls. It would seem to follow that since oxygen is more electro-negative than nitrogen the amino-ethers should be more stable than the acetals, whereas the reverse is the case and for the reason which has been stated above. Striking confirmation of this view is to be found in the observation that whereas diethylaminomethyl *n*-butyl ether (I) is readily decomposed by water, its methochloride (II) is remarkably stable and resists hydrolysis even in dilute acid solution at 100°. This substance is indeed much more stable than an acetal and the obvious explanation is that the nitrogen is now positively charged,

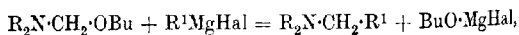


and instead of the condition $\overset{+}{\text{N}}-\overset{+}{\text{C}}\text{O}$ we have $\overset{+}{\text{N}}-\overset{+}{\text{C}}-\text{O}$, which should facilitate reduction to $\overset{+}{\text{N}}-\text{CH}$ rather than hydrolysis. The formation of methylamine, dimethylamine, and trimethylamine hydrochlorides from ammonium chloride and formaldehyde, and the process of methylation of amines by treatment with formaldehyde and formic acid are well-known examples of reactions in which such reduction actually occurs.

The quaternary ammonium hydroxide corresponding with the chloride II decomposes on heating with formation of methyldiethylamine and the indirect process of alkylation of secondary amines so indicated may prove serviceable in cases where there is a very great tendency towards the formation of quaternary salts. The stages recapitulated are:

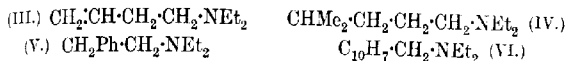


The reactivity of these dialkylaminomethyl ethers is, however, turned to much greater advantage in their condensation with organo-magnesium compounds. This occurs in accordance with the equation

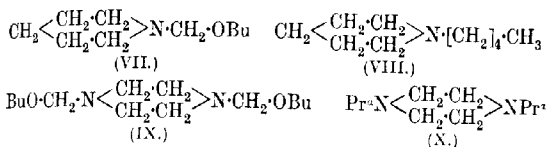


and the reactions were in all cases immediate and vigorous. Starting from diethylaminomethyl *n*-butyl ether (I), we have prepared

Δ^7 -butenyldiethylamine (III), δ -methyl-*n*-amyldiethylamine (IV), β -phenyltriethylamine (V), and α -homonaphthyldiethylamine (VI) by the action of magnesium allyl chloride, magnesium isoamyl bromide, magnesium benzyl chloride, and magnesium α -naphthyl bromide, respectively.



1-*n*-Butoxymethylpiperidine (VII) yields 1-*n*-amylypiperidine (VIII) on treatment with magnesium *n*-butyl iodide, and 1:4-di(*n*-butoxymethyl)piperazine (IX) is converted by magnesium ethyl bromide into 1:4-dipropylpiperazine (X).



The ease with which this reaction occurs again prompts a comparison with the acetals, which are unaffected by the Grignard solutions under ordinary conditions. Even orthoformic ester reacts sluggishly (Tschitschibabin, *Ber.*, 1904, **37**, 186; Bodroux, *Compt. rend.*, 1904, **138**, 92) and the reactivity which the oxygen in the amino-ethers displays towards magnesium appears explicable only on the basis of the constitutional theory which we have already advocated. Few reactions are more obviously connected with polar considerations than those of the organo-metallic compounds, and the behaviour of a substance towards magnesium methyl iodide can probably be used as a trustworthy guide to the extent to which polarisation* occurs in the molecule. Substances in which the atoms are held together by co-valencies only should react with difficulty if at all, whilst any pronounced polarisation should give rise to a reaction in view of the strong electropositive tendency of the magnesium atom. Judged by this criterion, the carbonyl group is polarised, that is, the carbon and oxygen are connected by a degree of electrovalency, which, however, does not necessarily amount to a full unit charge. This is in accordance with the theory put forward by Kermack and one of us (T., 1922, **121**, 427), since the oxygen octet is the more stable and the co-valency electrons are therefore appropriated by it to a certain unknown extent. In this case the bond is partly electrovalent. Such considerations do not apply to ethylene and its simple deriv-

* Synonymous are "partial dissociation," "electrovalency," "intramolecular ionisation."

atives and these in practice do not react with the Grignard reagents. Consequently ethylene should be represented as $\text{CH}_2\text{:CH}_2$ with co-valencies and not as $\overset{+}{\text{CH}_2}-\overset{-}{\text{CH}_2}$ — with one co-valency and one electrovalency, as recently suggested by Lowry who, however, does not, perhaps, propose to apply his view of the nature of the double linking to such a simple case.

If the symmetrical character of ethylene is disturbed by substitution, the induced polar effects may become so considerable that the unsaturated group simulates the behaviour of the carbonyl of a ketone. The bond is then clearly polarised, but, if chemical behaviour counts for anything, the extent to which the co-valencies are replaced by electrovalencies is variable. It is, for example, much greater in methylenemalonie ester than in benzylideneacetone and in the latter greater than in ethyl cinnamate. Mention should be made of the fact that methylamine condenses with formaldehyde and *n*-butyl alcohol in presence of potassium carbonate with formation of di(*n*-butoxymethyl)methylamine, $\text{NMe}(\text{CH}_2\text{OBu})_2$, which may prove to be a useful reagent in synthetical work. The equivalents of the new amino-ethers described were determined by decomposition with *N*/10-sulphuric acid and back-titration with *N*/10-sodium hydroxide, using methyl-orange as indicator.

EXPERIMENTAL.

Dimethylaminomethyl isoButyl Ether, $\text{CHMe}_2\text{CH}_2\text{OCH}_2\text{NMe}_2$.—An aqueous solution of dimethylamine (113 grams of 10 per cent.) was added with cooling to a mixture of *isobutyl* alcohol (20 grams) and formalin * (25 grams) and the whole saturated with potassium carbonate, well shaken, and allowed to remain over-night. The oil was then taken up in ether and the solution dried with potassium carbonate and distilled, using an efficient column. Thirteen grams of a colourless, mobile liquid boiling at $124\text{--}126^\circ/763$ mm. were obtained (Found: equivalent = 133; $\text{C}_7\text{H}_{17}\text{ON}$ requires equivalent = 131). The yield was therefore 40 per cent. of that required by theory and calculated on the dimethylamine employed, so that this experiment demonstrates that the formation of these ethers may occur in the presence of a considerable relative amount of water. Dimethylaminomethyl *isobutyl* ether is readily hydrolysed by dilute hydrochloric acid or by hot water with formation of its generators, and its odour is that of a mixture of these substances.

Diethylaminomethyl n-Butyl Ether (Formula 1).—Diethylamine

* Commercial so-called 40 per cent. formaldehyde. The methyl alcohol which this contains does not appear to give rise to the production of dialkylaminomethyl methyl ethers, probably because these substances are more rapidly hydrolysed than the similar ethers derived from higher alcohols.

(55 grams) was carefully added with cooling to formalin (85 grams) and after the addition of *n*-butyl alcohol (74 grams) the mixture was treated with so much potassium carbonate that about 10 grams remained undissolved. The whole was emulsified by vigorous shaking at intervals and after fifteen hours the oil was dissolved in ether and the solution dried by means of potassium carbonate. On fractionation under the ordinary pressure, 96.5 grams of a colourless, mobile liquid boiling at $172-174^{\circ}/754$ mm. were obtained. This is a yield of 80 per cent. of the theory calculated on the diethylamine employed (Found: equivalent = 158. $C_9H_{21}ON$ requires equivalent = 159). The properties of the substance closely resemble those of other members of this class of amino-ethers.

1-*n*-Butoxymethylpiperidine (Formula VII).—This substance was obtained from piperidine (42.5 grams), formalin (42 grams), and *n*-butyl alcohol (37 grams), following the method described in the foregoing sections. Sixty-five grams of an oil boiling at $210^{\circ}/772$ mm. were obtained. Distillation under ordinary pressure causes in this case slight decomposition and discoloration. The substance boils at $96^{\circ}/8$ mm. without decomposition (Found: equivalent = 172. $C_{10}H_{21}ON$ requires equivalent = 171). The substance is relatively stable towards water and is not immediately hydrolysed by cold dilute hydrochloric acid. Its odour is basic and the formaldehyde effect is only observed after an interval of a few seconds.

1:4-Di-*n*-butoxymethylpiperazine (Formula IX).—This substance was obtained by applying the general method to piperazine (32.5 grams), which was treated with formalin (85 grams), *n*-butyl alcohol (74 grams), and an excess of potassium carbonate. The ether, which resulted in a yield of 33 per cent. of the theory, is a colourless liquid boiling at $174^{\circ}/10$ mm. [Found: equivalent = 128. $C_{14}H_{30}O_2N_2$ (diacid base) requires equivalent = 129]. The original components are readily formed by hydrolysis in dilute acid solution and slowly by water alone.

Di(*n*-butoxymethyl)methylamine, $NMe(CH_2 \cdot OBu)_2$.—An aqueous solution of methylamine (21 grams of 20 per cent.) was added in one portion to a mixture of *n*-butyl alcohol (20 grams) and formalin (25 grams). The addition of the amine causes the separation of the liquid into two layers. So much potassium carbonate was then added that some of the salt remained undissolved and the mixture was frequently shaken and allowed to remain during two days. The oil was isolated in the usual manner and on distillation 12 grams of a colourless liquid boiling at $111^{\circ}/15$ mm. were obtained (Found: C = 64.7; H = 11.9. $C_{11}H_{25}O_2N$ requires

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C = 65.0; H = 12.3 per cent.). This interesting substance is readily hydrolysed by dilute acids with formation of methylamine, butyl alcohol, and formaldehyde, and in other respects behaves as a normal aminomethyl ether, but it gives inaccurate results on back-titration after decomposition with *N*/10-sulphuric acid. Possibly this may be due to the formation of a cyclic ester of sulphuric acid, but whether this explanation is the true one or is false the constitution of the compound is clearly that which has been assigned in view of the properties of the substance, the analytical results quoted, and the conversion to methyldiethylamine which is described below. It is proposed to attempt the utilisation of this derivative of methylamine for the synthesis of γ -piperidones by condensation with reactive derivatives of acetone.

Methyldiethyl-n-butoxymethylammonium Salts (Formula II).—Diethylaminomethyl *n*-butyl ether (8 grams) was mixed with methyl iodide (7 grams; 1.05 mol.) and kept in a dark cupboard in a closed vessel. The solution quickly became cloudy owing to the formation of the methiodide. In a few hours a considerable oily layer had separated and after three days the whole mass had become uniform and consisted of a yellow, viscous syrup which showed no tendency to crystallise. In order to remove small quantities of unchanged base and methyl iodide the material was twice washed with dry ether and then dissolved in water and converted into the corresponding chloride by treatment with an excess of freshly precipitated silver chloride, first during two hours in the cold, and then for fifteen minutes on the steam-bath. The filtered solution of the chloride was perfectly colourless and had no odour of formaldehyde. It may be kept unchanged for many weeks at room temperature and, even on boiling, hydrolysis occurs very slowly in neutral or acid media. On the addition of sodium hydroxide to the solution an oily ammonium hydroxide is precipitated and this on further heating decomposes with formation of butyl alcohol and methyldiethylamine (see below). The following derivatives are sparingly soluble oils; *periodide*, *perchlorate*, *mercurichloride*, *ferrichloride*, *ferricyanide*; the *chromate* and *oxalate* are readily soluble salts.

The *chloroplatinate* was found to be the most satisfactory derivative and was obtained in the usual manner as a voluminous buff precipitate. It is sparingly soluble in cold water, but dissolves freely in hot water and crystallises in frond-like aggregates of orange-yellow prisms which darken at 196° and melt at 204° with decomposition (Found: Pt = 26.0. $C_{20}H_{48}O_2N_2Cl_6Pt$ requires Pt = 25.8 per cent.).

Methyldiethylamine.—(A). The additive product from diethylaminomethyl *n*-butyl ether (20 grams) and an equal weight of

methyl iodide was dissolved in water, a little hydrochloric acid added, and steam passed through the solution. This was done under the impression that hydrolysis would be rapid and the butyl alcohol formed would then be conveniently removed. It transpired, however, that very little butyl alcohol was found in the distillate and even under these conditions only a small proportion of the quaternary salt suffered hydrolysis. Free iodine was removed from the solution by the addition of sulphurous acid and the liquid was then concentrated on the steam-bath to a syrup. This was mixed in a distilling flask with excess of concentrated aqueous potassium hydroxide and the mixture heated until no more base was evolved. The latter was collected in a vessel cooled by ice, and dried by means of potassium hydroxide and finally by distillation over successive small quantities of sodium. Ultimately 7.0 grams of the pure base boiling at 66° were obtained. Apparently no characteristic properties of derivatives of this simple amine (Passon, *Ber.*, 1891, 24, 1681) have yet been recorded.

The *chloroplatinate* is well adapted for the characterisation of the base and crystallises from ethyl alcohol in pale orange-yellow, prismatic needles melting sharply at 231° [Found: Pt = 33.36. $(C_5H_{13}N)_2 \cdot H_2PtCl_6$ requires Pt = 33.37 per cent.]. When the crystals in a moist condition were touched with a nickel spatula, the melting point was found to be considerably lowered and it is probably a desirable precaution in the manipulation of other platonic compounds to avoid all contact with foreign metals. The substance also crystallises from methyl alcohol in pale orange, rhombic prisms.

(B). An ethereal solution of magnesium methyl iodide was added to di(*n*-butoxymethyl)methylamine (4.5 grams) and ether (40 c.c.) until no further obvious reaction occurred. An efficient reflux condenser was attached to the flask in order to avoid loss of volatile base, and the mixture was allowed to remain for half an hour and then gently heated during ten minutes. Water was added to the product, which was then made strongly acid by means of hydrochloric acid. The ether was removed by distillation and steam passed through the residual aqueous solution until the distillate no longer contained butyl alcohol. The solution was cooled, rendered strongly alkaline, and again steam-distilled, the evolved base being collected by means of an adapter dipping in dilute hydrochloric acid. The acid solution was concentrated to a small bulk on the steam-bath and platonic chloride added. This produced a small precipitate of a chloroplatinate sparingly soluble in alcohol, which was collected and washed with alcohol. The mother-liquor and alcohol washings were combined and concentrated to

very small bulk. The main quantity of the chloroplatinate then separated on cooling and the substance was crystallised from ethyl alcohol and then again from methyl alcohol and obtained in rhombic prisms melting at 231° (Found : Pt = 33.35 per cent.). Comparison showed that the substance was identical with the chloroplatinate prepared as described under (A) above.

Benzyl-diethylamine Chloroplatinate.—A mixture of diethylamino-methyl *n*-butyl ether (7.9 grams) and benzyl chloride (6.3 grams) remained unchanged in the cold and was heated at 100° during seven hours. A brown oil separated and this became hard on cooling, but could not be crystallised. Water was added and steam passed through the solution, and as this did not effect decomposition of the quaternary salt the liquid was acidified with hydrochloric acid and evaporated to a small bulk on the steam-bath.

On the addition of sodium hydroxide and extraction with ether, very little base was obtained in the extract, but an insoluble oily quaternary ammonium hydroxide was thrown down. This was finally decomposed by distillation in a current of steam after the addition of an excess of sodium hydroxide, and the alkaline distillate was acidified with hydrochloric acid and concentrated. A somewhat sparingly soluble *chloroplatinate* was derived in the usual manner and crystallised readily from water in needles and then from methyl alcohol in pale buff, glistening plates melting at 203° [Found : Pt = 26.5. $(C_{11}H_{17}N)_2H_2PtCl_6$ requires Pt = 26.5 per cent.]. This salt has been previously prepared by Ladenburg and Struve (*Ber.*, 1877, 10, 47), but no description of the properties of the substance has yet been placed on record. It is very sparingly soluble in acetone or ethyl alcohol, somewhat more readily soluble in methyl alcohol or water.

Δ^1 -Butenyldiethylamine (Formula III).—A dilute ethereal solution of magnesium allyl chloride was gradually added to the diethylaminomethyl *n*-butyl ether (19 grams), dissolved in anhydrous ether. The addition of each drop produced a vigorous reaction and a curdy precipitate and it was easy to determine the point at which the whole of the amino-ether had been decomposed. After allowing to remain during a few hours, water was added in just sufficient amount to remove magnesium compounds from the ethereal solution, which was then filtered and the sludge of magnesium hydroxide washed with fresh ether in the flask. The combined filtrate was four times extracted with dilute hydrochloric acid and this acid solution concentrated to a small bulk. On cooling, the hydrochloride separated as a mass of deliquescent crystals. The base was separated by addition of concentrated aqueous potassium hydroxide and careful distillation of the

mixture. It was taken up in ether, the solution dried by means of potassium hydroxide and distilled. For analysis, a specimen was redistilled over sodium (Found: C = 75.3; H = 13.6. $C_8H_{17}N$ requires C = 75.6; H = 13.4 per cent.). This base is the diethyl analogue of the dimethylpyrrolidine, b. p. 89–92°, prepared by Ciamician and Magnaghi (*Gazzetta*, 1885, **15**, 485) by methylation of pyrrolidine. It is a mobile liquid with a characteristic odour and boils at 132°/767 mm. The addition of alcoholic picric acid to the base produces a precipitate of the *picrate* in golden-yellow needles melting at 60°. When this amine is mixed with methyl iodide, the *methiodide* immediately separates in solid form and to the accompaniment of a crackling sound. The substance dissolves in water and is converted into the oily quaternary hydroxide by treatment with an excess of potassium hydroxide. This decomposes but slowly on heating and with production of butadiene and methyldiethylamine.

δ-Methyl-n-amyl-diethylamine (Formula IV).—The preparation of this substance followed in all its details that of butenyldiethylamine, magnesium allyl chloride being replaced by magnesium *isocamyl* bromide. No crystalline hydrochloride was obtained, however, and after the addition of potassium hydroxide to the concentrated solution of the hydrochloride the base was at once extracted by ether. Ten grams of diethylaminomethyl *n*-butyl ether gave 5 grams of the pure amine boiling at 172° (Found: C = 76.1; H = 14.8. $C_{10}H_{23}N$ requires C = 76.4; H = 14.6 per cent.). Most of the salts of this base are very readily soluble and some of the sparingly soluble double salts, for example, the *mercurichloride*, obtained in oily drops, could not be crystallised. The *chloroplatinate*, however, crystallises from methyl alcohol, in which it is somewhat readily soluble, in pale orange, rectangular prisms melting at 101°.

1-n-Amylpiperidine (Formula VIII).—A solution of magnesium *n*-butyl iodide, prepared from *n*-butyl iodide (16 grams) and magnesium (2.2 grams) in ether (120 c.c.), was gradually added to 1-*n*-butoxymethylpiperidine (9 grams), dissolved in ether (20 c.c.). After half an hour, the mixture was gently heated and then cooled and a small amount of water added so as to decompose the magnesium compounds dissolved in the ether. The filtered solution was shaken with successive small portions of dilute hydrochloric acid and the combined extracts were concentrated on the steam-bath. The crystalline residue of the hydrochloride was mixed with concentrated aqueous potassium hydroxide and ether, and solid potassium hydroxide added until the aqueous layer was saturated. The separated ethereal solution was then dried by the further

action of the reagent and distilled. The base boiled at $196^{\circ}/769$ mm. and at $80^{\circ}/8$ mm. (Found: C = 77.6; H = 13.6. $C_{10}H_{21}N$ requires C = 77.4; H = 13.5 per cent.). The *picrate* crystallises from ethyl alcohol in bright yellow, prismatic needles melting at 107° . It is sparingly soluble in ether or water and readily soluble in methyl alcohol, acetone, or benzene.

1 : 4-*Dipropylpiperazine* (Formula X).—This substance was prepared in the usual manner from 1 : 4-di(*n*-butoxymethyl)piperazine and an excess of magnesium ethyl bromide and the reaction was immediate and vigorous. The base, obtained in a yield of 70 per cent. of that theoretically possible, was distilled finally over sodium. It boils without decomposition at $206^{\circ}/762$ mm. and is an inodorous liquid which does not crystallise at 0° (Found: C = 70.5; H = 12.9. $C_{10}H_{22}N_2$ requires C = 70.6; H = 12.9 per cent.). On the addition of picric acid, dissolved in alcohol, to an alcoholic solution of the base the *monopicate* is first precipitated in intense yellow crystals, but this gives place to the *dipicate*, which is very much more sparingly soluble.

This characteristic derivative is practically insoluble in boiling ethyl or butyl alcohol, but crystallises from hot acetic acid, in which it is also sparingly soluble, in bright yellow, hair-like needles which darken at 250° and melt at 258° with decomposition (Found: C = 42.1; H = 4.2. $C_{22}H_{28}O_{11}N_8$ requires C = 42.0; H = 4.4 per cent.).

3-*Phenyltriethylamine* (Formula V).—Diethylaminomethyl *n*-butyl ether (24 grams), diluted with an equal volume of ether, was cautiously added to an ethereal solution of magnesium benzyl chloride (21 grams of benzyl chloride, 4.4 grams of magnesium). When the vigorous reaction was finished, the mixture was gently heated during a few minutes and the base isolated in the usual manner and finally purified by distillation in a vacuum. The colourless oil boils at $103^{\circ}/8$ mm. and not quite without decomposition at $223^{\circ}/763$ mm. (Found: C = 81.5; H = 10.8. $C_{12}H_{19}N$ requires C = 81.4; H = 10.7 per cent.). The odour of this substance is faintly basic and also recalls that of phenylethyl alcohol. It combines readily with methyl iodide to a viscid, yellow liquid which crystallises on standing, and this *methiodide*, which is very readily soluble in alcohol and moderately soluble in benzene, crystallises from ethyl acetate in elongated, rectangular plates showing a tendency to twin and melting at 109° . The substance was dissolved in water and the solution rendered strongly alkaline by means of potassium hydroxide. The quaternary ammonium hydroxide which separated decomposed readily on heating and the products were removed by distillation in steam. Styrene, b. p.

144°/772 mm., and methyl-diethylamine chloroplatinate were isolated and readily identified.

α-Homonaphthyl-diethylamine (Formula VI).—This substance was prepared from *α*-bromonaphthalene (20 grams), magnesium (2.7 grams), and diethylaminomethyl *n*-butyl ether (15.3 grams) in precisely the manner described above in the case of *β*-phenyltriethylamine. Nine grams of base boiling at 160°/9 mm. were obtained. The boiling point under the ordinary pressure is 293° (Found: C = 84.3; H = 9.0. $C_{15}H_{19}N$ requires C = 84.5; H = 8.9 per cent.). The *picrate* is very much more readily soluble in hot than in cold alcohol and separates in beautiful clusters of golden-brown needles or from acetone in yellow, silky needles melting at 136–137°.

We desire to express our thanks to the Food Investigation Board for grants which have enabled one of us (G. M. R.) to take part in this investigation.

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[Received, January 6th, 1923.]

LXVI.—*Preparation and Reactions of Bromopicrin.*

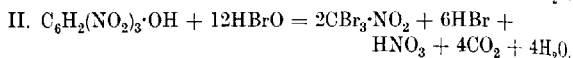
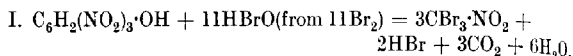
By LOUIS HUNTER.

BROMOPICRIN was first prepared by Stenhouse (*Annalen*, 1854, **91**, 307) by distillation of an aqueous mixture of picric acid, lime, and bromine. This method was repeated by Bolas and Groves (this *Journal*, 1870, **23**, 153), who claim that the conversion of picric acid into bromopicrin according to the scheme $C_6H_2(NO_2)_3 \cdot OH \rightarrow 3CBr_3 \cdot NO_2$ is almost quantitative. According to Scholl and Brenneisen (*Ber.*, 1898, **31**, 654), however, the product contains a small admixture of dibromodinitromethane.

Orton and McKie (*T.*, 1921, **119**, 29) were successful in modifying the Stenhouse-Hofmann process for the preparation of chloropierin to suit laboratory and industrial conditions. The process described in the present paper is an attempt to apply the results of these authors to the case of bromopierin. Archetti (*Boll. Chim. farm.*, 1903, **42**, 673) states that exposure of aqueous picric acid and bromine to direct sunlight for several months produces a yellow oil. This experiment has been repeated and the oil found to be impure bromopierin. By working in the presence of sodium carbonate the time of exposure can be reduced to a few days, and a

suitable choice of conditions ensures a good yield of practically pure bromopierin. In the absence of light, the reaction proceeds in the same way, but requires a somewhat longer period for completion.

The reaction follows a course similar to that proposed by Orton and McKie (*loc. cit.*) in the case of chloropierin, hypobromous acid or its sodium salt being the active agent.



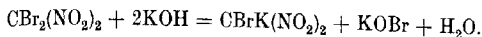
Measurements of the amount of bromine required to decompose a known weight of picric acid, and estimations of bromide and bromate produced during the reaction, give results which are in close agreement with the above equations. Equation I indicates the reappearance as bromopierin of the whole of the nitro-groups present in the picric acid; the yield in this case would amount to 390 per cent. calculated on the original picric acid. Equation II requires a yield of 260 per cent., the remainder of the nitrogen appearing as nitric acid. Estimations of the nitrate-content of the liquors by the Schulze-Tiemann method serve as a means of measuring the extent to which the reaction follows equation II. Under the best conditions—a faintly alkaline medium—the yield of bromopierin can be raised to 353 per cent., the proportion of nitrate in the liquors being correspondingly small.

When prepared in an acid or in a strongly alkaline medium, bromopierin is formed only in poor yield, much of the picric acid remaining unchanged even after long exposure (see Table I).

The chief impurity contained in the crude oil is carbon tetrabromide, arising either by the further bromination of bromopierin, or directly by bromination of the non-nitrated carbon atoms in the picric acid molecule. In no case does the amount of carbon tetrabromide in the crude bromopierin exceed 0.5 per cent. Since such small amounts do not materially alter the figures for total bromine, the carbon tetrabromide is detected only by such reactions as involve bromopierin but leave the tetrabromide unaffected. The reaction with caustic alkali has been used to estimate carbon tetrabromide in the crude oil.

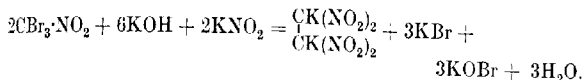
Reaction with Concentrated Alkali.—It was observed by Wolff and Rüdel (*Annalen*, 1897, **294**, 201) that bromopierin reacts vigorously with 50 per cent. caustic potash to form potassium bromide and a yellow explosive salt. Although this salt was not examined by them, they suggested that it was the potassium salt of bromonitromethane, from analogy with the case of dibromo-

dinitromethane (Losanitsch, *Ber.*, 1882, **15**, 471), which is attacked by caustic potash as follows :



Investigation of the reaction, however, has shown this suggestion to be incorrect. The yellow salt is bromine-free, and is the *s*.-dipotassium tetranitroethane which was obtained by Scholl and Brenneisen (*Ber.*, 1898, **31**, 642) by the action of alcoholic potassium cyanide on bromopicrin.

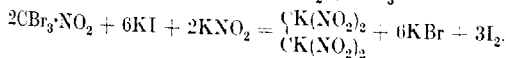
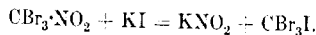
The yellow precipitate obtained by the action of concentrated potash on bromopicrin contains large quantities of potassium bromide and bromate, and the actual yield of the organic salt is small. Its formation is the result of a series of simultaneous reactions, the effect of which may be expressed thus :



The nitrite is supplied by side-decompositions of the bromopicrin; for example, $\text{CBr}_3\cdot\text{NO}_2 + 6\text{KOH} = 3\text{KBr} + \text{KNO}_2 + \text{K}_2\text{CO}_3 + 3\text{H}_2\text{O}$. Potassium hypobromite is present in considerable quantity in the filtrate.

Attempts to obtain the corresponding sodium salt in a pure state by a similar method were unsuccessful owing to its much greater solubility. That the reaction with concentrated sodium hydroxide is exactly parallel, however, is shown by the formation of a yellow, explosive precipitate containing bromide and having properties similar to those of the potassium salt.

Reaction with Potassium and Sodium Iodides.—In the same paper, Wolff and Rüdel state that bromopicrin liberates iodine from aqueous or alcoholic solutions of potassium iodide with formation of a yellow, crystalline, explosive salt. Repetition of this work reveals the fact that the explosive salt in this case also is *s*.-dipotassium tetranitroethane. The reaction may be compared with that between bromopicrin and aqueous alcoholic potassium cyanide (Scholl and Brenneisen, *loc. cit.*), yielding the same potassium salt together with potassium bromide and cyanogen bromide. A series of equations similar to those put forward by these authors may be suggested and summarised thus :

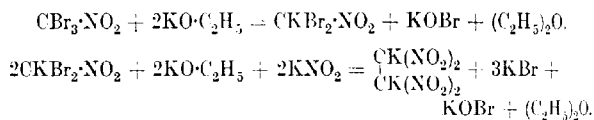


After standing for some hours, the alcoholic filtrate from the

potassium salts deposits crystals of potassium nitrate, without doubt produced by oxidation of the potassium nitrite.

With alcoholic sodium iodide, bromopierin liberates iodine and produces a yellow solid containing the corresponding sodium salt. The extreme solubility of the latter makes its isolation in the pure state impossible.

Reaction with Sodium and Potassium Ethoxides.—It has been shown by Röse (*Annalen*, 1880, 205, 249) that chloropierin reacts with alcoholic sodium ethoxide with formation of ethyl orthocarbonate. The yield, however, is not good, and under the best conditions amounts only to 30 per cent. of the theoretical. It was thought, therefore, that the use of bromopierin in a similar reaction might lead to a more satisfactory yield of orthocarbonate. This proves not to be the case, however, only traces of orthocarbonate being formed and a yellow mixture containing bromide, bromate, and an organic salt precipitated. As in the previous experiments, the sodium salt proves too soluble for isolation; but by use of potassium ethoxide an organic potassium salt can be obtained, which by its properties and analysis is shown to be *s*.-dipotassium tetranitroethane. An intermediate mixture of organic salts, the analysis of which suggests the presence of potassium dibromonitromethane, has been isolated; and consequently the course of the reaction is represented thus:



As before, the nitrite is generated by side-decompositions of the bromopierin. The ether is obtained as a first fraction in the recovery of alcohol from the filtrate.

In the hope of attributing the low yield of ethyl orthocarbonate—at least partly—to the formation of similar organic salts in the reaction between sodium ethoxide and chloropierin, the salt mixture obtained from this reaction was examined. Very small amounts of organic salts were obtained, hence this contributes in only a small degree to the poorness of yield of orthocarbonate.

In the various reactions of bromopierin described above, the equations are not to be regarded as an exact representation of the changes going on, since side-reactions are known to occur. The low yield of the organic potassium salt together with the high proportion of bromide found in the crude mixtures points to other and more complete decompositions of the bromopierin molecule.

EXPERIMENTAL.

Bromopicrin.—Picric acid (10 grams) and sodium carbonate (60 grams) were dissolved in a litre of water, and bromine (26 c.c.) was added. The mixture was exposed to sunlight for a period of five to seven days, when the colour had faded to a light yellow and the layer of bromine had been replaced by a yellowish-brown oil. Longer exposures are not to be recommended, since diminution of yield occurs. The oil was removed in a current of steam, washed several times with aqueous caustic soda followed by water, and finally dried over anhydrous sodium sulphate. The product was practically pure bromopicrin. Yield 35 grams (Found: Br = 80.73. Calc., Br = 80.54 per cent.). It gave the following constants: m. p. 9.7—10.3°, d_4^{20} 2.799, $[R_L]_D^{20}$ 35.51 ($\text{CBr}_3\cdot\text{NO}_2$ requires 36.08).

Table I indicates the yield of bromopicrin and the time required for the completion of the reaction under various conditions, the end of the reaction being judged roughly by the fading of the bromine colour. The table refers to 10 grams of picric acid, 26 c.c. of bromine, and 1000 c.c. of water. The equivalent proportions of sodium carbonate are calculated on the weight of picric acid used.

TABLE I.

	Yield of bromopicrin per cent.	Time of reaction.
No sodium carbonate	285	6 weeks
5 equivs. Na_2CO_3 (11.6 grams)	330	3 "
10 " Na_2CO_3 (23.2 ")	342	10—14 days
15 " Na_2CO_3 (34.7 ")	342	10 "
20 " Na_2CO_3 (46.3 ")	350	7 "
25 " Na_2CO_3 (57.9 ")	353	5 "
30 " Na_2CO_3 (69.6 ")	353	5 "
100 grams NaOH	190	2 weeks
100 " H_2SO_4	146	Unfinished after 8 weeks

s.-Dipotassium Tetranitroethane, $\begin{matrix} \text{C}(\text{NO}_2)_2\text{NO}\cdot\text{OK} \\ \text{C}(\text{NO}_2)_2\text{NO}\cdot\text{OK} \end{matrix}$ (a) By the action

of caustic potash. Bromopicrin was slowly added in small amounts to a cooled solution of potassium hydroxide ($\text{KOH}:\text{H}_2\text{O} = 1:1$). A pale yellow solid immediately separated and the oil became semi-solid. After a short time, a violent reaction commenced with considerable heating and further separation of the yellow salt. The precipitate contained potassium bromide and bromate together with the organic salt. Owing to the comparative insolubility of potassium bromate, numerous crystallisations from water were necessary to obtain the pure organic salt, thus entailing great loss. By addition of carbamide to the reaction mixture no bromate is formed, and there is no need for repeated crystallisation.

To 5 grams of carbamide, dissolved in 50 c.c. of 50 per cent. caustic potash, 25 grams of bromopicrin were slowly added with cooling. The precipitate was washed with alcohol, and thereafter two crystallisations from hot water yielded a pure product. Yield of crude mixture (uncrystallised), 18 grams. Yield of pure dipotassium tetranitroethane, 0.5 gram.

s.-Dipotassium tetranitroethane prepared in this way is a bright yellow, crystalline powder, most easily crystallised from aqueous alcohol. It explodes on heating at $269-273^{\circ}$, or by contact with strong acids (Found: K = 27.3; N = 19.33. Calc., K = 27.3; N = 19.58 per cent.).

(b) *By the action of potassium iodide.* Twenty-five grams of potassium iodide were dissolved in 500 c.c. of 90 per cent. alcohol. On addition of bromopicrin, a yellow, crystalline precipitate was immediately formed and iodine liberated. Considerable rise of temperature was observed. Addition of bromopicrin was continued in small amounts until a test portion of the liquor no longer gave a precipitate with bromopicrin. The amount of bromopicrin required was 33 grams. The precipitate, consisting of potassium bromide and the organic potassium salt, was collected, washed with alcohol, and dried. Yield 12 grams. Two crystallisations from water yielded pure dipotassium tetranitroethane (2.3 grams), explosion point 272° (Found: K = 27.13; N = 19.03 per cent.).

(c) *By the action of potassium ethoxide.* To 12 grams of potassium, dissolved in 150 c.c. of absolute alcohol, 25 grams of bromopicrin, dissolved in 30 c.c. of alcohol, were slowly added with frequent cooling, a cream-coloured precipitate immediately forming. When the addition of bromopicrin was complete, the mixture was warmed cautiously on the water-bath until a vigorous ebullition set in. At this stage the precipitate changed colour to orange and a considerable quantity of nitrogen was evolved. When the reaction had moderated, the mixture was boiled on the water-bath for half an hour, cooled, and filtered. Yield 33 grams. Two crystallisations from hot water gave 0.8 gram of the pure salt, explosion point $269-273^{\circ}$ (Found: K = 27.39 per cent.).

A reaction similar to that with potassium ethoxide is obtained by use of alcoholic potash, but the yield of pure salt is not good. Carbamide or phenylhydrazine may be used to facilitate reaction, although the yield of the salt is not appreciably increased.

s.-Dipotassium tetranitroethane, prepared by any of the above methods, exhibits general properties which agree with those of the salt described by Scholl and Brenneisen (*loc. cit.*). It was further identified with this compound by its decomposition with acids, yielding dinitromethane; the preparation of the corresponding

silver salt (Found: Ag = 51.2. Calc., Ag = 50.9 per cent.); and its bromination in aqueous solution, yielding tribromotrinitroethane (Found: Br = 58.9. Calc., Br = 59.7 per cent.).

Table II compares the yield of dipotassium tetranitroethane when prepared by the various methods. Potassium cyanide is the reagent used by Scholl and Brenneisen, the yield of the organic salt having been worked out from the method of preparation given by these authors. The table shows that the most convenient and economical method for the preparation of *s.*-dipotassium tetranitroethane is by use of potassium iodide.

TABLE II.

Reagent.	Bromopierin.	Crude product.	Pure salt.
KOH (50 grams)	25 grams	18 grams	0.5 gram
KI (18.8 grams).....	25 "	8.2 "	1.5 grams
KOEt (K 12 grams)	25 "	33 "	0.8 gram
KCN (23.5 grams)	25 "	9.5 "	1.7 grams

Estimation of Carbon Tetrabromide in the Crude Bromopierin.—

A known weight of the crude oil is decomposed with 50 per cent. caustic potash or soda. The precipitated solid is filtered through a porous crucible and washed with alcohol. On diluting the washings with water, the whole of the carbon tetrabromide contained in the original oil is precipitated. It is collected, dried, and weighed. After one crystallisation from alcohol, a specimen melted at 92—93° (Found: Br = 96.3. Calc., Br = 96.4 per cent.). Using this method of estimation, it is found that the crude oil contains least carbon tetrabromide when prepared in an alkaline medium: and that protracted exposure to light, especially with excess of bromine, tends to increase the proportion of carbon tetrabromide.

The author wishes to express his thanks to Professor K. J. P. Otton, F.R.S., for his help and criticism.

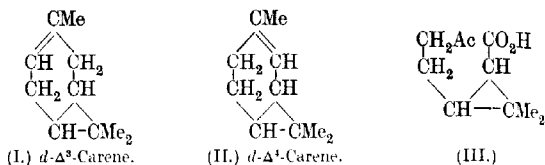
UNIVERSITY COLLEGE OF NORTH WALES,
BANGOR.

[Received, January 30th, 1923.]

LXVII.—*The Constituents of Indian Turpentine from Pinus longifolia, Roxb. Part II.*

By JOHN LIONEL SIMONSEN and MADYAR GOPAL RAU.

In Part I of this series (T., 1920, 117, 570) the isolation of a new bicyclic terpene was described and it was suggested that the constitution of this interesting hydrocarbon, to which the name *d.*-carene was given, was represented by either formula I or II.



It was not at the time found possible to decide definitely which of these two formulæ correctly represented the constitution of the terpene, although formula I (*d*- Δ^3 -carene) was considered the more probable. The evidence adduced in favour of this formula may be summarised as follows: (i) on treatment with hydrogen chloride, a mixture of dipentene and sylvestrene dihydrochlorides resulted; (ii) on oxidation with potassium permanganate in alkaline solution at 0°, a glycol, $C_{10}H_{18}O_2$, and dimethylmalonic acid were obtained; (iii) oxidation in hot alkaline solution with potassium permanganate yielded *trans*-caronic acid; and (iv) the molecular refraction was normal, indicating the absence of any conjugated system.

A recent investigation of the terpene isolated from the essential oil from *Andropogon Jwarancusa*, Jones (I., 1922, **121**, 2292) has shown that this terpene is in all probability *d*- Δ^4 -carene (II). This conclusion was based on a study of its reaction with hydrogen chloride, when dipentene and sylvestrene dihydrochlorides were formed, and by the fact that on oxidation in acetone solution with potassium permanganate there resulted a keto-acid, $C_{10}H_{16}O_3$, which there can be little doubt was 1:1-dimethyl-2- γ -ketobutylcyclopropane-3-carboxylic acid (III). It may further be mentioned that this hydrocarbon, unlike the hydrocarbon from *P. longifolia*, had a very high molecular refraction.

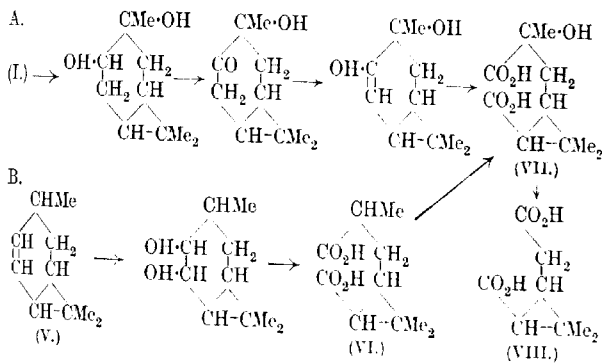
Since the oxidation of *d*- Δ^4 -carene proceeded very smoothly in acetone solution, we decided to investigate the behaviour of *d*- Δ^3 -carene under similar experimental conditions in the hope of isolating an isomeric keto-acid of the formula $C_{10}H_{16}O_3$. Contrary to our expectation, no trace of a keto-acid appeared to be formed, a very complex mixture of acids resulting. A prolonged examination of these has, in our opinion, definitely proved that the hydrocarbon under investigation cannot possibly be represented by formula II and is therefore *d*- Δ^3 -carene (I).

The separation of the oxidation products was a matter of considerable difficulty and is described in detail in the experimental portion of this paper (p. 554). It was found possible to separate (i) dimethylmalonic acid, (ii) *as*-dimethylsuccinic acid, (iii) *cis*- and *trans*-caronic acids, (iv) a *dibasic* acid, $C_8H_{12}O_4$, m. p. 136–137°, and (v) two *levorotatory* hydroxy-dibasic acids, $C_{10}H_{16}O_5$, m. p. 133°.

and 192°. In addition to these crystalline acids, which could not unfortunately be separated in large quantity, considerable amounts of liquid and resinous acids were formed which it has not up to the present proved possible to purify.

The two hydroxy-acids, which were quite stable to potassium permanganate in alkaline solution, were found to be α -hydroxy-acids, since on oxidation with an acid solution of potassium permanganate they were converted quantitatively with loss of carbon dioxide into two isomeric keto-acids of the formula $C_9H_{14}O_3$. Unfortunately neither of the keto-acids could be induced to crystallise, but they were readily distinguished by the preparation of the semicarbazones. The α -acid (m. p. 133°) gave a keto-acid which yielded a semicarbazone melting at 179–180°, whilst the semicarbazone of the keto-acid derived from the β -acid (m. p. 192°) decomposed at 209°. The former semicarbazone was optically inactive, whereas the latter showed a strong laevorotation, a point which will be referred to subsequently.

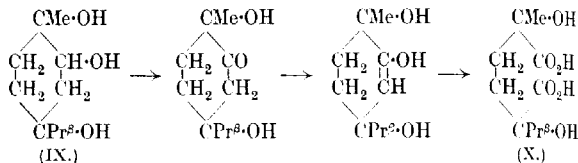
It was at once obvious that the two hydroxy-dibasic acids must be represented by formula VII and at first it appeared to us possible that *d*-carene was the Δ^2 -derivative (V), oxidation having proceeded in accordance with scheme B.



Careful consideration has, however, led to the conclusion that it is extremely unlikely that *d*-carene can be represented by formula V. The following appear to us to be cogent arguments against the acceptance of this formula: (i) oxidation of the glycol (*loc. cit.*, p. 571) with chromic acid does not appear to yield a diketone, since the oxidation product does not react with *o*-phenylenediamine. Thus no evidence for the presence of two secondary alcohol groups in the glycol was obtained. (ii) A dibasic acid of formula VI could

not be detected amongst the products of the oxidation. (iii) The formation of dipentene and sylvestrene dihydrochlorides by the action of hydrogen chloride would require a molecular rearrangement. (iv) A hydrocarbon of formula V would be expected to show a high molecular refraction, since the double linking is conjugated with the cyclopropane ring.

In the authors' opinion, there can be little doubt that the oxidation has proceeded in accordance with scheme A. Although the mechanism is somewhat unusual, it is not without analogy, since Wallach (*Annalen*, 1907, **356**, 206; 1908, **362**, 263) has shown that 1:2:4-trihydroxyterpane (IX) on oxidation with potassium permanganate yielded $\alpha\alpha'$ -dihydroxy- α -methyl- α' -isopropyladipic acid (X), the oxidation having proceeded as formulated below.

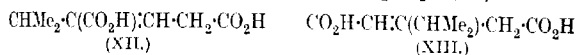
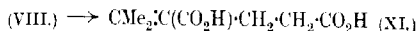


Owing to the very limited quantity of the hydroxy- and dibasic acids which could be separated in a pure state, it was unfortunately not found possible to examine their properties in any detail. The α -hydroxy-acid (m. p. 133°), which was found to be slightly levorotatory, gave, when heated with acetyl chloride, a *lactone* melting at 174–175°, whilst at the same time partial isomerism to the β -acid, melting at 192°, took place. From the fact that it yielded a lactone, from which the original acid was regenerated on treatment with alkali, it may be assumed that the hydroxy-group and carboxyl group were in the *cis*-position, but no further evidence as to its configuration was obtained.

The β -acid was not attacked by acetyl chloride, being recovered unchanged after prolonged treatment with this reagent. Attention has already been directed to the observation that the semicarbazone obtained from the keto-acid derived from the α -hydroxy-acid (m. p. 133°) was optically inactive, whereas that derived from the isomeric β -acid (m. p. 192°) was optically active. From this the conclusion may be drawn that the inactive semicarbazone (m. p. 179–180°) is the semicarbazone of the *cis*-keto-acid, since, as has been clearly shown by Aschan ("Chemie der alicyclischen Verbindungen," p. 439) in the case of the *cis*- and *trans*-forms of caronic acid, the *cis*-acid is incapable of resolution. The active semicarbazone, m. p. 209°, must therefore be derived from the *trans*-keto-acid. This theoretical conclusion was partly confirmed experimentally.

When the *cis*-keto-acid was oxidised with alkaline hypobromite solution, a dibasic acid, m. p. 136—137°, was formed which was identical with the dibasic acid $C_8H_{12}O_4$ referred to above as having been isolated directly from the mixture of oxidation acids. This acid, for which the name *homocaronic acid* (VIII) is proposed, was found to be a *cis*-acid, since it readily yielded an *anhydride* when treated with acetyl chloride. Unfortunately, the *trans*-keto-acid was not obtained in sufficient quantity for the preparation of the corresponding *trans*-homocaronic acid.

It was not found possible to obtain direct evidence for the constitution of *cis*-homocaronic acid and of the presence of the *cyclo*-propane ring. When treated with hydrogen bromide at 100°, a viscid oil resulted which was free from terpenylic acid, since it gave a readily soluble barium salt. Although the acid was not acted upon by bromine in either chloroform or acetic acid solution, its alkaline solution was somewhat readily attacked by potassium permanganate in the cold. It is not impossible that this property is due to the fact that the cyclic acid tends to isomerise to one of the corresponding unsaturated acids XI, XII, or XIII, a type of reaction which is now being studied by Thorpe and his collaborators in a notable series of researches (T., 1922, 121, 651 and subsequent papers).



It is hoped to attempt the preparation of these acids synthetically, and in the meantime the formula for *cis*-homocaronic acid cannot be considered as definitely established, although the simultaneous formation of *cis*-caronic acid would appear to support the correctness of the formula.

The remaining products isolated from the mixture of oxidation acids, *as*.-dimethylsuccinic acid and dimethylmalonic acid, require no comment, since they represent the final products formed by the degradation of the *cyclo*propane ring structure.

EXPERIMENTAL.

To the terpene (40 c.c.), dissolved in pure acetone (400 c.c.) and kept at 0°, finely powdered and sieved potassium permanganate (96 grams) was gradually added, with vigorous stirring. Oxidation proceeded slowly, and approximately forty-eight hours were required for the addition of the permanganate. When oxidation was complete the manganese dioxide was separated and well washed with acetone. It was then repeatedly extracted with boiling water until

the filtrate was perfectly colourless, at least ten extractions being required. The deep brown extract was concentrated on the water-bath to a small bulk in a current of carbon dioxide. After extraction with ether to remove a small quantity of neutral oxidation products, the solution was made acid with dilute sulphuric acid, when a brown oil separated. The oxidation acids were extracted with ether, five extractions being made in the usual manner, and the remainder of the very soluble acids obtained by extraction in a constant-extraction apparatus. The combined ether extracts were dried and the ether evaporated, when a deep brown, viscid oil was obtained which smelt strongly of acetic acid (yield 110 grams from 200 c.c. of terpene).

In order to separate the acids they were converted into the esters, and as the yield by the usual method of esterification was poor the following method was adopted with satisfactory results. The crude acid, mixed with alcohol (200 c.c.) and sulphuric acid (20 c.c.), was heated on the water-bath in an apparatus provided with a fractionating still-head while alcohol vapour (from 2 litres of alcohol) was passed through the mixture (compare Ingold and Nickolls, T., 1922, 121, 1643). The ethereal extract of the esters was washed with sodium carbonate solution, dried with potassium carbonate, the ether evaporated, and the residual oil distilled under diminished pressure (yield 92 grams *).

The esters consisted of a very complex mixture and it was not found possible to separate any fraction of constant boiling point. Ultimately the following fractions were obtained at 67 mm.: (a) below 150°, (b) 150—180°, (c) 180—190°, (d) 190—200°, (e) 200—220°.

Fraction (a) (B. p. below 150°/67 mm.).—This fraction, which weighed only 2 grams, was a colourless, mobile oil with a pleasant smell. The acid, obtained by hydrolysis with alcoholic potassium hydroxide and extraction with ether in the usual manner, separated immediately as a crystalline solid. After draining on porous porcelain, which removed a trace of adherent oil (probably *isobutyric* acid), it was found to decompose at 186°. It crystallised from benzene in prisms which decomposed at 190° with slight previous softening and was identified as dimethylmalonic acid by the method of mixed melting point.

Fraction (b) (B. p. 150—180°/67 mm.).—This fraction (29 grams) gave on analysis C = 64.9; H = 8.9 per cent. After hydrolysis with alcoholic potassium hydroxide and extraction with ether,

* The yield of ester was nearly quantitative, since the sodium carbonate washings only contained 1 gram of acid. The alcohol distillate contained a quantity of ethyl acetate and also of a second ester, possibly ethyl *isobutyrate*.

a viscid, yellow oil was obtained which, on keeping, slowly partly crystallised. The mixture of acids was found to be best separated in the following manner. The acids were converted into the ammonium salt, and the aqueous solution evaporated to dryness on the water-bath and finally kept for some days in a vacuum desiccator over sulphuric acid until completely anhydrous. On trituration of the ammonium salt with absolute alcohol, a crystalline solid separated; this was collected (A) and the filtrate once more evaporated on the water-bath to remove the alcohol. The residual oil was dissolved in water, made faintly alkaline with ammonia, and boiled with excess of calcium chloride solution, when a sparingly soluble salt (B) was precipitated. The filtrate obtained after removal of the calcium salt was acidified and the organic acids were recovered by extraction with ether (C).

The sparingly soluble ammonium salt (A) (1.3 grams) was decomposed with dilute sulphuric acid, and the crystalline acid which was deposited taken up with ether, and the ether evaporated, when a solid remained which melted at 211—212°. It crystallised from water in prisms melting at 213° and was identified as *trans*-canonic acid by analysis (Found: C = 53.3; H = 6.5. Calc., C = 53.2; H = 6.3 per cent.) and by the method of mixed melting point.

The sparingly soluble calcium salt (B) yielded an acid which crystallised from toluene in needles melting at 138—140° and was identified as *as*-dimethylsuccinic acid by the method of mixed melting point.

The crude mixture of acids (C), on keeping for some days in a vacuum desiccator, partly crystallised. After trituration with benzene, the crystals were collected and boiled with chloroform, when a colourless, crystalline solid remained which decomposed at 174—175°. This melting point was unaltered by recrystallisation from water and the acid was identified as *cis*-canonic acid by analysis (Found: C = 53.4; H = 6.4. Calc., C = 53.2; H = 6.3 per cent.) and by conversion into terebic acid by heating with hydrobromic acid at 100°.

The liquid acids which remained after the separation of the *cis*-canonic acid deposited no further solid on keeping and were mixed with an excess of acetic anhydride and heated at 220° for six hours in a sealed tube. After removing the acetic anhydride by distillation at the ordinary pressure, the residue was distilled at 17 mm., when three fractions were obtained: (i) 100—150°, (ii) 150—180°, (iii) 180—200°. A considerable tarry residue remained in the distillation flask which decomposed on further heating. The three fractions, which were insoluble in cold sodium carbonate solution, were reconverted into the corresponding acids. Fraction (i) was

found to consist solely of caronic anhydride; fraction (ii) consisted mainly of caronic anhydride mixed with a small amount of a second acid. The *cis*-caronic acid was readily separated in a pure state by conversion into the ammonium salt and precipitation of the latter from alcoholic solution with ether. From the ether-alcohol solution a second acid was recovered, but not in sufficient quantity for examination.

Fraction (iii) was found to be only very slowly hydrolysed by hot water. It was therefore treated with a hot aqueous solution of sodium hydroxide and the acid recovered in the usual manner by extraction with ether. The viscid oil thus obtained crystallised partly on keeping. After trituration with benzene, the solid was collected and recrystallised from hot water, from which it separated in rosettes of needles melting at 137° . It was identified as *cis*-homocaronic acid (see below) by the method of mixed melting point.

The benzene solution from which *cis*-homocaronic acid had been separated yielded on evaporation a considerable quantity of liquid acids which could not be purified.

Fraction (c) (B. p. $180-190^{\circ}/67$ mm.).—This fraction (17 grams), which consisted of a somewhat viscid, faintly yellow oil, was hydrolysed with alcoholic potassium hydroxide solution and the acid isolated by extraction with ether. On long keeping in the ice chest, the viscid, brown oil thus obtained slowly deposited a small quantity of a crystalline solid. This was washed with benzene and purified by repeated crystallisation from hot water and finally from toluene.

cis-Homocaronic acid (VIII) crystallised from hot water in very characteristic rosettes of prismatic needles which melted at $136-137^{\circ}$, and this melting point was not altered by further crystallisation. It was only sparingly soluble in chloroform, benzene, or cold water, readily in hot water or hot toluene (Found: C = 55.9; H = 6.7. $C_8H_{12}O_4$ requires C = 55.8; H = 7.0 per cent.). The acid did not yield satisfactory results on titration, but the silver salt, which separated from a faintly alkaline solution as a caseous white precipitate, gave a correct value (Found: Ag = 55.8. $C_8H_{10}O_4Ag_2$ requires Ag = 55.9 per cent.). The reason for the unsatisfactory results obtained on titration could not be determined.

cis-Homocaronic acid was not attacked by bromine in either chloroform or acetic acid solution even on warming; when it was dissolved in a dilute solution of sodium carbonate and treated with a drop of potassium permanganate solution, the colour was somewhat rapidly discharged at 0° . When the acid was heated with acetyl chloride on the water-bath for a short time, and the excess of acid chloride removed in a vacuum over potassium hydroxide,

a viscid oil was obtained which was insoluble in hot water or cold alkalis. It evidently consisted of the *anhydride* and when boiled with water for some time gradually dissolved, the original acid (m. p. 136—137°) crystallising from the aqueous solution on cooling.

The viscid oil from which the *cis*-homocaronic acid had been separated could not be induced to crystallise. After treatment with acetyl chloride, a small quantity of β -1-*x*-hydroxy-3-carboxy- α :1:1-trimethylcyclopropane-2-propionic acid (see below) was isolated, but the bulk of the product could not be obtained crystalline.

Fraction (d) (B. p. 190—200°/67 mm.).—This fraction on redistillation was found to boil mainly at 184—185°/45 mm. (Found: C = 62.3; H = 8.7. $C_{14}H_{24}O_5$ requires C = 61.7; H = 8.8 per cent.). After hydrolysis with alcoholic potassium hydroxide solution, an acid was obtained as a viscid brown oil, from which fine needles slowly deposited. The separation of the mixture of isomerides offered much difficulty owing to the presence of resinous impurities. The partly crystalline oil was triturated with cold water and the sparingly soluble portion (A) separated by filtration through a hardened filter-paper. The filtrate was evaporated on the water-bath and finally completely dehydrated in a vacuum desiccator over sulphuric acid, when the residual oil partly solidified. After grinding with a small quantity of benzene, the crystals were collected and purified by repeated crystallisation from benzene. The original filtrate (B) was reserved for later investigation.

α -1-*x*-Hydroxy-3-carboxy- α :1:1-trimethylcyclopropane-2-propionic acid (VII) crystallised from benzene in well-formed, glistening prisms which melted at 132—133°. It was extremely readily soluble in water and in all the ordinary organic solvents with the exception of benzene and light petroleum. In alkaline solution it was stable to potassium permanganate solution (Found: C = 55.5; H = 7.4; $M = 215$. $C_{10}H_{16}O_5$ requires C = 55.6; H = 7.4 per cent.; $M = 216$). In chloroform solution, the acid was slightly levorotatory, $[\alpha]_D = -8.7^\circ$.

The *silver* salt separated from a faintly alkaline solution as a remarkably gelatinous precipitate which could be filtered and washed only with difficulty. It darkened somewhat rapidly on exposure to light (Found: Ag = 49.8. $C_{10}H_{14}O_5Ag_2$ requires Ag = 50.2 per cent.).

The sparingly soluble acid fraction (A) (see above) was dissolved in hot water and the solid which separated purified by crystallisation from dilute methyl alcohol. β -1-*x*-Hydroxy-3-carboxy- α :1:1-trimethylcyclopropane-2-propionic acid (VII) crystallised in glistening prisms which melted at 192° and decomposed slightly above this

temperature. It was very much more sparingly soluble in all the ordinary solvents than the α -acid (Found: C = 55.8; H = 7.2; $M = 215$. $C_{10}H_{16}O_5$ requires C = 55.6; H = 7.4 per cent.; $M = 216$). In chloroform solution, $[\alpha]_D - 24.36^\circ$ was observed. In alkaline solution, the acid was found to be stable to a solution of potassium permanganate.

The benzene filtrate (B) (see above) from which the α -acid had been separated was, after removal of the solvent, heated on the water-bath for some time with an excess of acetyl chloride. After evaporating the acetyl chloride in a vacuum over potassium hydroxide, a brown resinous oil remained from which a small further quantity of the β -acid was obtained, but the bulk of the oil could not be crystallised.

Action of Acetyl Chloride on α -1- α -Hydroxy-3-carboxy- α :1:1-trimethylcyclopropane-2-propionic Acid.

In one experiment, the α -hydroxy-acid (1 gram) was mixed with acetyl chloride (5 c.c.) and heated on the water-bath for one hour. After removing the acetyl chloride and acetic acid, a crystalline solid remained which melted indefinitely at 145° . On fractional crystallisation from benzene, an acid was obtained in glistening leaflets which melted at 174 – 175° (Found: C = 60.9; H = 6.9. $C_{10}H_{14}O_4$ requires C = 60.6; H = 7.1 per cent.). The lactone of the α -hydroxy-acid was extremely readily soluble in cold water and on titration with cold barium hydroxide solution was found to behave as a monobasic acid (Found: $M = 198$. Calc., $M = 198$). It was unfortunately not obtained in sufficient quantity for a molecular-weight determination, but was in all probability the δ -lactone of the hydroxy-acid. When boiled with alkali, it was reconverted into the hydroxy-acid, but it could be crystallised unchanged from water.

From the benzene from which the lactone had been crystallised an acid was obtained in small quantity which melted at 192° and was identified as the β -acid, which had been formed by isomerisation of the α -acid.

Oxidation of α - and β -1- α -Hydroxy-3-carboxy- α :1:1-trimethylcyclopropane-2-propionic Acids.

cis-1:1-Dimethyl-2- β -ketopropylcyclopropane-2-carboxylic Acid.—As the result of a number of comparative experiments the following method was found to yield the most satisfactory results. The α -hydroxy-acid (1 gram), dissolved in water (5 c.c.), was gradually treated with a mixture of potassium permanganate (0.28 gram), sulphuric acid (0.28 gram), and water (6 c.c.), the temperature

being kept at about 40° during the addition. Oxidation took place readily with evolution of carbon dioxide, and after warming at 70° for a short time the clear reaction mixture was saturated with ammonium sulphate, when a colourless oil separated. This was taken up with ether and the ether dried and evaporated. The viscoid oil, which showed no signs of crystallising even when kept for some weeks, evidently consisted of the *cis*-keto-acid, since on treatment with semicarbazide acetate it was converted quantitatively into the *semicarbazone*. The *semicarbazone*, which was somewhat sparingly soluble in cold water, more readily in hot, crystallised from dilute methyl alcohol in small plates which sintered at 177° and decomposed at 179 – 180° (Found: C = 53.1; H = 7.8. $C_{10}H_{17}O_3N_3$ requires C = 52.9; H = 7.5 per cent.). In acetic acid solution it was found to be optically inactive.

When the keto-acid was oxidised with sodium hypobromite solution under the same conditions as were used for the oxidation of *d*-1:1-dimethyl-2- γ -ketobutylcyclopropane-3-carboxylic acid (*loc. cit.*, p. 2297), a quantitative yield of *cis*-homocaronic acid, melting at 136 – 137° , was obtained. This acid was found to be identical in every way with the specimen of *cis*-homocaronic acid isolated directly from the oxidation of *d*- Δ^3 -carene.

1. *trans*-1:1-Dimethyl-2- β -ketopropylcyclopropane-2-carboxylic Acid.—This acid was obtained as a very viscoid, colourless oil when the β -acid was oxidised with an acid solution of potassium permanganate under the same conditions as were used for the oxidation of the α -acid, except that owing to the sparing solubility of the acid it was found convenient to keep the temperature at 70° during the whole reaction.

On treatment with semicarbazide acetate the *semicarbazone* separated as a very sparingly soluble, crystalline powder, which was purified by recrystallisation from a mixture of alcohol and acetic acid. It crystallised in beautiful, hexagonal prisms which, when rapidly heated, decomposed at 209° (Found: C = 53.1; H = 7.8. $C_{10}H_{17}O_3N_3$ requires C = 52.9; H = 7.5 per cent.). In acetic acid solution, it was found to be strongly levorotatory, $[\alpha]_D^{20} = -70.98^{\circ}$ being observed.

Unfortunately the *trans*-keto-acid was obtained in insufficient quantity for conversion into the corresponding dibasic acid.

Fraction (e) (B. p. 200 – $220^{\circ}/0.7$ mm.).—This fraction, which consisted of a very viscoid, brown oil, yielded on hydrolysis an extremely resinous acid. It was found possible by extraction with cold water to separate a small quantity of the α -hydroxy-acid, but the greater portion consisted of an uncrystallisable resin.

The authors wish to take this opportunity of expressing their indebtedness to Mr. Guest, Manager of the Government Turpentine Factory, Jallo, Punjab, for supplying them with large quantities of pure turpentine.

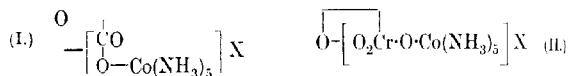
FOREST RESEARCH INSTITUTE AND COLLEGE,
DEHRA DUN.

[Received, January 9th, 1923.]

LXVIII. *Complex Metallic Ammines. Part VIII.*
The Introduction of Di- and Tri-basic Organic
Acid Radicles into the Pentamminecobaltic
Complex.

By JAMES COOPER DUFF.

CARBONATOPENTAMMINECOBALTIC salts differ from the normal type of acidopentammine salts in that only one limb of the carbonate radicle is directly linked to cobalt in the co-ordination sphere, and it is usual to regard the other limb as attached to the complex in the form of a "bound" ion, as in formula I.



Other salts of this type which have been definitely characterised are the chromato-, sulphato-, sulphito-, and oxalato-salts.

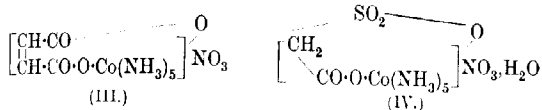
The introduction of dibasic organic acid radicles, other than oxalate, in a similar form does not appear to have been described hitherto, or has not previously been found to be possible. The methods used by Jörgensen (*Z. anorg. Chem.*, 1896, **11**, 426) for the oxalatopentamminecobaltic salts have been tested with malonic acid and the other acids of the same series, but without the desired result. It has, however, been found possible to use two methods, namely (1) the reaction between the dibasic acid and carbonatopentamminecobaltic nitrate and (2) a modification of the method used by Briggs (*T.*, 1919, **115**, 69) for the formation of chromatopentamminecobaltic salts (formula II) in which use is made of the reaction between potassium chromate and aquopentamminecobaltic salts.

The two methods adopted gave two new series of complex salts which are discussed separately below; the results obtained by using the two tribasic acids, citric and orthophosphoric, in a similar way are also mentioned.

The Reaction between the Sodium Salts of the Oxalic Acid Series and Aquopentamminecobaltic Nitrate.

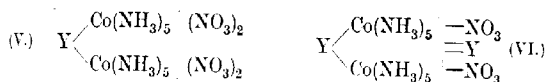
Briggs (*loc. cit.*) used a very dilute solution of aquopentamminecobaltic nitrate for the reaction with potassium chromate. In the present series it was found necessary to work with a concentrated solution, and also to have a moderately high concentration of sodium salt. The resulting salts fall into three classes:

(1) Acidopentammine nitrates of the carbonato-type (formula I) are given by only two sodium salts, those of maleic and sulphoacetic acids. The two nitrates are therefore represented by formulæ III and IV:



Sodium oxalate displaced all the nitrate and gave aquopentamminecobaltic oxalate.

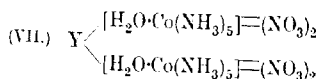
(2) This class is a series of nitrates of a new complex type represented by formula V.



Y represents the dibasic acid radicle of the following acids:—malonic, maleic, malic, phthalic, citraconic, itaconic, glutaric, and adipic acids.

Following Werner's method of nomenclature, these salts may be regarded as decamminediacobaltic nitrates. In this class it is convenient to include the two salts (formula VI) derived from sodium mesotartrate and sodium methionate. In the former, which contains $4\text{H}_2\text{O}$, Y is $\text{C}_2\text{H}_2(\text{OH})_2(\text{CO}\cdot\text{O})_2$, and in the methionate Y is $\text{CH}_2(\text{SO}_2\cdot\text{O})_2$.

(3) Aquopentammine salts only were obtained from the sodium salts of succinic, tartaric, and fumaric acids. They are represented by VII, in which Y is the dibasic acid radicle.

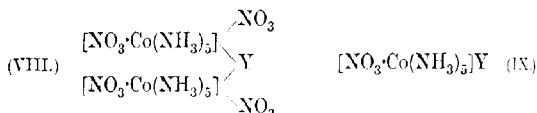


The carboxyl groups of these three acids are much more averted from each other than those of the acids in the former two classes. This arrangement, and the comparative solubilities of the possible products, undoubtedly affect the nature of the substance obtained in each case. In this connexion it will be noticed that the three

acids, malonic, sulphoacetic, and methionic, when used in the form of their sodium salts, all behave differently, thus illustrating the modifying influence of a sulphonic group when it has replaced a carboxyl group.

It will be seen that only two new salts of the type of formula I have been obtained by this method. The salts in class (2) require special notice. They are all mauve pink, microcrystalline salts which are only moderately soluble in water. They hydrolyse slowly to aquopentammine salts. Dilute nitric acid precipitates aquopentamminecobaltic nitrate from their aqueous solutions. These properties show that they bear little, if any, resemblance to the usual types of decammine salts described by Werner (*Ber.*, 1908, 41, 3916) in the series of decammine- μ -aminodicobaltic salts and other similar polynuclear compounds. The present series thus really belongs to the pentammine type of salts, and it is proposed to name them as acidodipentamminecobaltic salts.

The constitution indicated by formula V is based on the following evidence: (a) The results of analysis, the estimation of nitrate being of most importance. (b) The absence of water indicates that the salts are not aquopentammine salts. This is also supported by the conductivity results. (c) The existence of the isomeric form with nitrate in the complex (formula VIII) is improbable,



since there is no evidence that a nitrate radicle will enter the complex in a warm neutral solution of what is essentially an aquopentammine nitrate at the beginning. Even if this were probable, the resulting compound would be of the type IX, which does not agree with any of the salts obtained, except perhaps those from sodium mesotartrate and sodium methionate (compare formula VI). (d) The organic acids represented in this series of compounds all have a structure which brings their carboxyl groups close together in space. (e) The compounds are not mixtures of isomerides, since in several of the preparations the first crystals that separated and those that were subsequently deposited gave the same results on analysis. There was one exception to this, the maleato-salts; the first separation corresponded to formula V, but the crystals which separated afterwards consisted entirely of the compound represented by formula III.

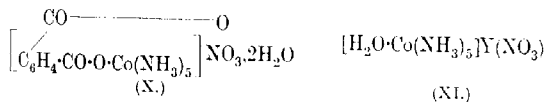
It is not clear why these various acid radicles should enter and constitute part of the co-ordination complex. Briggs (*loc. cit.*)

considered the formation of chromatopentammine salts to be due to the considerable residual affinity of the chromate radicle, which enables it to displace the water in the aquopentammine complex. He did not start with pure aquopentammine salts, but prepared these in solution from the corresponding acidopentammine salts. The author has found that an aqueous solution of a pure aquopentammine salt, whilst it is suitable for making the chromatosalts, is not capable of giving pure salts of types III and V; the product always contains some aquo-salt, as shown by its high conductivity in solution. On the other hand, by starting with the carbonatopentammine nitrate and preparing the aquopentammine nitrate in solution from this, there is no difficulty in obtaining salts which are free from aquo-salts. Possibly the presence of sodium nitrate in the solution causes a state of equilibrium between nitratopentammine nitrate and aquopentammine nitrate. The organic radicle may then replace the nitrate in the complex and thus cause the formation of more of the nitrate-salt until the reaction with the organic sodium salt is complete. It may be mentioned, in support of such a possibility, that although the dipentammine salts are only slightly soluble they separate very slowly from solution, a good yield being obtained in some cases only after several weeks. Further evidence on this point is given in the note at the end of the paper.

The Reaction between Acids of the Oxalic Acid Series and Carbonatopentamminecobaltic Nitrate.

The results obtained in this type of reaction can also be divided into three classes:

1. The salts represented by formulæ III and IV are again given by maleic and sulphoacetic acids. Phthalic acid also comes unexpectedly into this class, as it yields phthalatopentamminecobaltic nitrate (X).

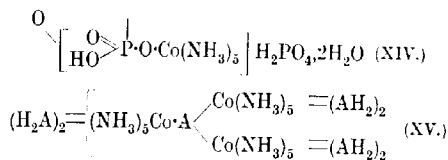


Mesotartaric acid also gives a salt which is apparently similar in type but less stable in solution, the mesotartrate radicle leaving the complex as a result of hydrolysis; this explanation of the instability has been confirmed by conductivity measurements (compare the evidence previously obtained with a mesotartrato-salt, T., 1922, 121, 452).

The salts of this class resemble carbonatopentamminecobaltic

aquopentammine nitrate gives a different compound from the above in the case of the citrate which has much higher conductivity values, and even higher values when aquopentammine chloride is used as the starting material. These facts emphasise the labile nature of the nitrate radicle in the special solution used for the preparations, a point which has a bearing on the nature of the compounds formed from dibasic acids.

When orthophosphoric acid reacts with carbonatopentamminecobaltic nitrate, the product is orthophosphatopentamminecobaltic dihydrogen phosphate (XIV).



where $\text{A} = \text{C}_6\text{H}_5\text{O}_7$.

Citric acid reacts readily with the carbonatopentamminecobaltic nitrate to give a very sparingly soluble salt which has been identified as citratotri-pentamminecobaltic dihydrogen citrate (XV). The formation of this unusual polynuclear complex seems quite possible, since there will be no interference with its production if the middle carboxyl group in citric acid is averted from the other two.

EXPERIMENTAL.

Salts Derived from Aquopentamminecobaltic Nitrate.

The following method applies to all the salts which come under this heading. The details are given here to save repetition.

Five grams of carbonatopentamminecobaltic nitrate, 20 c.c. of water, and 20 c.c. of 2 N-nitric acid were maintained at 45° until effervescence ceased. The solution was neutralised with 2N-sodium hydroxide and at once treated with the sodium salt (1 mol.) under investigation, dissolved in water (20 c.c.) at 45°. Having been maintained at 45° for twenty minutes, the solution was filtered, and, after the addition of 8 c.c. of ethyl alcohol, left at room temperature for a week or more, when the crystals which had separated were collected. The majority of the salts form microscopic, rose-pink crystals and are sparingly soluble in cold water. Cobalt was estimated as the anhydrous sulphate, ammonia by distillation with sodium hydroxide solution, and nitrate by reduction to ammonia and subsequent distillation with alkali.

Aquopentamminecobaltic oxalate, $[\text{H}_2\text{O} \cdot \text{Co}(\text{NH}_3)_5]_2(\text{C}_2\text{O}_4)_3 \cdot 4\text{H}_2\text{O}$, was obtained in minute, brick-red crystals in very good yield. It

was found to be identical with that prepared by Jörgensen (*Z. anorg. Chem.*, 1898, 17, 461) from chloropentamminecobaltic chloride (Found: Co = 18.01; NH₃ = 25.43; C₂O₄ = 40.38. Calc., Co = 17.86; NH₃ = 25.75; C₂O₄ = 40.00 per cent.).

Oxalatopentamminecobaltic nitrate,
$$\begin{array}{c} \text{CO} \text{---} \text{O} \text{---} \text{O} \\ | \qquad \qquad \qquad | \\ [\text{CO} \cdot \text{O} \cdot \text{Co}(\text{NH}_3)_5] \text{NO}_3 \cdot 2\text{H}_2\text{O} \end{array}$$
 was prepared from the above oxalate as follows: 3.3 grams of aquopentamminecobaltic oxalate, dissolved in 200 c.c. of water at 90°, having been treated with barium nitrate (1.3 grams; 1 mol.) in 20 c.c. of water, the solution was immediately cooled, filtered, and evaporated at 70° to about 25 c.c. The nitrate separated in minute, brick-red crystals. Yield = 1.8 grams. The salt is moderately soluble in cold water and gives no precipitate with calcium chloride until ammonia solution is added or the solution heated (Found: Co = 17.89; NH₃ = 25.28; NO₃ = 19.01; C₂O₄ = 26.78. C₂H₁₅O₇N₆Co₂·2H₂O requires Co = 17.87; NH₃ = 25.75; NO₃ = 18.79; C₂O₄ = 26.66 per cent.).

Malonatodipentamminecobaltic nitrate [V, with Y = CH₂(COO)₂] was obtained in minute, rose-red, elongated plates. Yield = 2 grams after three weeks (Found: Co = 18.18; NH₃ = 25.78; NO₃ = 38.08; H₂O = 3.05. C₃H₃₂O₁₆N₁₁Co₂·H₂O requires Co = 17.98; NH₃ = 25.91; NO₃ = 37.80; H₂O = 2.74 per cent.). The aqueous solution gives a precipitate with barium chloride only after boiling. Potassium chromate gives a brownish-yellow precipitate of a chromate.

Sulphoacetatopentamminecobaltic nitrate (IV) was obtained in a yield of 2.2 grams (Found: Co = 16.55; NH₃ = 23.29; NO₃ = 16.99. C₂H₁₇O₈N₆SCo₂·H₂O requires Co = 16.29; NH₃ = 23.48; NO₃ = 17.12 per cent.).

The salt is only moderately soluble in water and the aqueous solution gives no precipitate with potassium chromate.

Methionatodipentamminecobaltic nitrate methionate (VI) was obtained in a yield of 3.6 grams (Found: Co = 15.50; NH₃ = 22.34; NO₃ = 16.45. C₂H₃₁O₁₈N₁₂S₂Co₂ requires Co = 15.52; NH₃ = 22.37; NO₃ = 16.32 per cent.). The aqueous solution gives with potassium chromate a brownish-yellow, crystalline precipitate which is both a nitrate and a chromate.

Mesotartatodipentamminecobaltic nitrate mesotartate (VI) was obtained in a yield of 3.3 grams (Found: Co = 15.03; NH₃ = 21.55; NO₃ = 15.55. C₈H₃₅O₁₈N₁₂Co₂·4H₂O requires Co = 15.12; NH₃ = 21.78; NO₃ = 15.89 per cent.). The salt does not lose water at 100°. A warm aqueous solution gives with potassium chromate a brownish-yellow precipitate which is both a nitrate and a chromate.

Aquopentamminecobaltic tartrate dinitrate [VII, with $Y = C_2H_2(OH)_2(CO \cdot O)_2$] was obtained in brownish-red aggregates of small, rhombic crystals. Yield = 3.5 grams (Found: Co = 16.14; $NH_3 = 23.65$; $NO_3 = 33.98$. $C_4H_{38}O_{26}N_{14}Co_2$ requires Co = 16.38; $NH_3 = 23.61$; $NO_3 = 34.44$ per cent.). A warm aqueous solution reacts with potassium chromate to give brown crystals of chromatopentamminecobaltic nitrate.

Aquopentamminecobaltic succinate dinitrate (VII) was obtained in small, brownish-red, rhombic crystals. Yield = approx. 3.5 grams (Found: Co = 17.16; $NH_3 = 24.92$; $NO_3 = 36.40$. $C_4H_{38}O_{18}N_{14}Co_2$ requires Co = 17.14; $NH_3 = 24.71$; $NO_3 = 36.05$ per cent.). The salt is only sparingly soluble in cold water but more readily on heating. A warm solution gives, with potassium chromate, chromatopentamminecobaltic nitrate as in the case of the tartrate above.

Aquopentamminecobaltic fumarate dinitrate (VII, with $2H_2O$, where $Y = CO_2 \cdot CH:CH \cdot CO_2$), was obtained in a yield of 3.2 grams (Found: Co = 16.65; $NH_3 = 22.99$; $NO_3 = 33.55$; $H_2O = 2.51$. $C_4H_{38}O_{18}N_{14}Co_2 \cdot 2H_2O$ requires Co = 16.33; $NH_3 = 23.41$; $NO_3 = 34.35$; $H_2O = 4.98$ per cent.). The salt is moderately soluble in water and immediately gives a precipitate of silver fumarate with silver nitrate. Potassium chromate, added to the aqueous solution, gives crystals of chromatopentammine nitrate. The salt loses only half its water of crystallisation at 100° .

Maleatodipentamminecobaltic nitrate (V, with $Y = CO_2 \cdot CH:CH \cdot CO_2$) was obtained in a yield of 1 gram (Found: Co = 18.05; $NH_3 = 26.10$; $NO_3 = 38.07$. $C_4H_{32}O_{16}N_{14}Co_2$ requires Co = 18.14; $NH_3 = 26.15$; $NO_3 = 38.15$ per cent.). The salt is only moderately soluble in warm water, and must be heated for some time with barium chloride to give a precipitate of barium maleate. Potassium chromate gives a brownish-yellow precipitate of a chromate.

Maleatopentamminecobaltic nitrate (III) was obtained when the filtrate from the previous salt, having been reheated at 60° for thirty minutes, was left for three weeks to crystallise. Yield 1.8 grams (Found: Co = 18.20; $NH_3 = 26.44$; $NO_3 = 19.20$. $C_4H_{17}O_7N_6Co$ requires Co = 18.44; $NH_3 = 26.53$; $NO_3 = 19.37$ per cent.). It is moderately soluble in water and unlike the previous salt gives no precipitate with potassium chromate.

Maleatodipentamminecobaltic nitrate [V, with $Y = CO_2 \cdot CH(OH) \cdot CH_2 \cdot CO_2$] was obtained in a yield of 2 grams (Found: Co = 17.43; $NH_3 = 25.14$; $NO_3 = 35.77$. $C_4H_{34}O_{17}N_{14}Co_2$ requires Co = 17.65; $NH_3 = 25.44$; $NO_3 = 35.62$ per cent.). Addition of potassium chromate to a warm aqueous solution causes the separation of a brown chromate.

Phthalatodipentamminecobaltic nitrate [V, with $Y = C_6H_4(CO-O)_2$] was obtained in a yield of 2.4 grams (Found: Co = 16.93; $NH_3 = 26.45$; $NO_3 = 35.81$. $C_8H_{34}O_{16}N_{14}Co_2$ requires Co = 16.85; $NH_3 = 24.29$; $NO_3 = 35.43$ per cent.). The salt is moderately soluble in warm water. It gives no reaction for phthalate until after hydrolysis with aqueous ammonia. Potassium chromate, added to the aqueous solution, gives a brownish-yellow precipitate of a chromate.

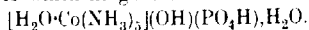
Citraconatodipentamminecobaltic nitrate (V, with $Y = CO_2-CMe:CH-CO_2$) was obtained in a yield of 1.5 grams (Found: Co = 17.83; $NH_3 = 25.29$; $NO_3 = 37.98$. $C_5H_{34}O_{16}N_{14}Co_2$ requires Co = 17.76; $NH_3 = 25.60$; $NO_3 = 37.35$ per cent.). The aqueous solution, treated with potassium chromate, gives a brownish-yellow precipitate of a chromate.

Itaconatodipentamminecobaltic nitrate [V, with $Y = CO_2-C(CH_3)-CH_2-CO_2$] was obtained in a yield of 1.3 grams (Found: Co = 17.68; $NH_3 = 25.34$; $NO_3 = 37.43$. $C_5H_{34}O_{16}N_{14}Co_2$ requires Co = 17.76; $NH_3 = 25.60$; $NO_3 = 37.35$ per cent.). With potassium chromate, its aqueous solution gives an almost insoluble brownish-yellow chromate.

Glutaratodipentamminecobaltic nitrate (V, with $Y = CO_2-(CH_2)_3-CO_2$) was obtained in a yield of 1.6 grams (Found: Co = 17.86; $NH_3 = 25.44$; $NO_3 = 37.13$. $C_5H_{36}O_{16}N_{14}Co_2$ requires Co = 17.71; $NH_3 = 25.53$; $NO_3 = 37.24$ per cent.). It reacts with aqueous potassium chromate to give a brownish-yellow chromate.

Adipatodipentamminecobaltic nitrate (V, with $Y = CO_2-(CH_2)_4-CO_2$) is similar to the glutarate-salt (Found: Co = 17.18; $NH_3 = 25.05$; $NO_3 = 36.97$. $C_6H_{38}O_{16}N_{14}Co_2$ requires Co = 17.34; $NH_3 = 25.00$; $NO_3 = 36.47$ per cent.).

Orthophosphatopentamminecobalt (XII) was obtained in brick-red, flattened needles by using a solution of 6.73 grams of hydrated disodium hydrogen phosphate to which 18.75 c.c. of *N*-sodium hydroxide had been added to make a solution of trisodium phosphate. Yield 3 grams (Found: Co = 21.26; $NH_3 = 31.03$; $PO_4 = 34.16$. $H_{15}O_4N_5PCo_2 \cdot 2H_2O$ requires Co = 21.44; $NH_3 = 30.91$; $PO_4 = 34.54$ per cent.). The salt does not lose water at 100°. It is only sparingly soluble in warm water. The solution gives a precipitate with silver nitrate but not with ferric chloride. Jørgensen (*J. pr. Chem.*, 1885, [ii], 31, 83) described an aquopentamminecobaltic orthophosphate to which he gave the formula



This salt loses $2H_2O$ at 100° and the method of preparation also distinguishes it from the above salt.

Citratopentamminecobalt (XIII) was obtained in minute, pink crystals. Yield 2.8 grams from 6.1 grams of potassium citrate, used with the cobaltammine reagent [Found: Co = 15.89; NH_3 = 22.55; $\text{C}_6\text{H}_5\text{O}_7$ = 51.51. $\text{C}_6\text{H}_5\text{O}_7\text{N}_3\text{Co}\cdot 2\text{H}_2\text{O}$ requires Co = 15.97; NH_3 = 23.03; $\text{C}_6\text{H}_5\text{O}_7$ = 51.22 per cent.]. The salt is only sparingly soluble in warm water. No water of crystallisation is lost at 100° . Citrate was estimated by boiling with excess of standard sodium hydroxide, filtering, and titrating the residual sodium hydroxide with standard sulphuric acid.

Salts Derived from Carbonatopentamminecobaltic Nitrate.

The following general method was used for all the acids investigated in this series. Five grams of carbonatopentamminecobaltic nitrate, mixed with 10 c.c. of water, were treated with a solution of the acid (1 mol.) in 30 c.c. (or more if necessary) of water at 60° . The filtered solution was evaporated to about 25 c.c. at 60° , and, on standing over-night, the desired salt usually separated. The salts, the majority of which again form microscopic, rose-pink crystals, are arranged below in three classes.

1. Salts related to carbonatopentamminecobaltic nitrate. *Maleatopentamminecobaltic nitrate* (III) and *sulphonacetatopentamminecobaltic nitrate* (IV) were both again obtained (see pp. 566, 567) (Found: for the former, Co = 18.32; NH_3 = 26.58; NO_3 = 19.14; for the latter, Co = 16.40; NH_3 = 23.43; NO_3 = 17.29 per cent.).

Phthalatopentamminecobaltic nitrate (X) was obtained in a yield of 3.2 grams (Found: Co = 14.89; NH_3 = 21.03; NO_3 = 15.65; H_2O = 8.70. $\text{C}_8\text{H}_5\text{O}_7\text{N}_3\text{Co}\cdot 2\text{H}_2\text{O}$ requires Co = 14.53; NH_3 = 20.93; NO_3 = 15.27; H_2O = 8.82 per cent.). It is moderately soluble in cold water and gives no precipitate with potassium chromate.

Mesotartratopentamminecobaltic nitrate.

$[\text{C}_2\text{H}_2(\text{OH})_2(\text{CO}\cdot\text{O})_2\text{Co}(\text{NH}_3)_5]\text{NO}_3\cdot 3\text{H}_2\text{O}$, was obtained in a yield of 3.2 grams (Found: Co = 14.65; NH_3 = 20.96; NO_3 = 15.48. $\text{C}_4\text{H}_5\text{O}_9\text{N}_3\text{Co}\cdot 3\text{H}_2\text{O}$ requires Co = 14.45; NH_3 = 20.83; NO_3 = 15.19 per cent.). It is moderately soluble in cold water and hydrolyses somewhat readily, being converted by potassium chromate into chromatopentamminecobaltic nitrate.

Oxalic acid gives the same result as sodium oxalate in the previous series, aquopentamminecobaltic oxalate again being formed (Found: Co = 17.95; NH_3 = 25.61; C_2O_4 = 40.36 per cent.). The oxalato-nitrate is described in the previous series.

2. Dipentamminecobaltic salts having the general formula VI.
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Malonatopentamminecobaltic malonate nitrate was obtained in minute, purple-red crystals (Found: Co = 17.79; NH_3 = 25.94; NO_3 = 18.86; H_2O = 5.72. $\text{C}_6\text{H}_{33}\text{O}_{14}\text{N}_{12}\text{Co}_2\cdot 2\text{H}_2\text{O}$ requires Co = 18.09; NH_3 = 26.07; NO_3 = 19.01; H_2O = 5.52 per cent.).

Malatodipentamminecobaltic malate nitrate was obtained in a yield of 2.6 grams (Found: Co = 17.36; NH_3 = 25.10; NO_3 = 18.22. $\text{C}_8\text{H}_{38}\text{O}_{16}\text{N}_{12}\text{Co}_2$ requires Co = 17.44; NH_3 = 25.15; NO_3 = 18.34 per cent.).

Citraconatodipentamminecobaltic citraconate nitrate was obtained in a yield of 1.2 grams (Found: Co = 16.76; NH_3 = 24.64; NO_3 = 17.97. $\text{C}_{10}\text{H}_{38}\text{O}_{14}\text{N}_{12}\text{Co}_2\cdot 2\text{H}_2\text{O}$ requires Co = 16.75; NH_3 = 24.15; NO_3 = 17.61 per cent.).

Itaconatodipentamminecobaltic itaconate nitrate was obtained in a yield of 1.1 grams (Found: Co = 17.53; NH_3 = 25.57; NO_3 = 18.65. $\text{C}_{10}\text{H}_{38}\text{O}_{14}\text{N}_{12}\text{Co}_2$ requires Co = 17.66; NH_3 = 25.45; NO_3 = 18.56 per cent.).

Glutaratodipentamminecobaltic glutarate nitrate was obtained in a yield of 1.9 grams (Found: Co = 17.70; NH_3 = 25.24; NO_3 = 18.41. $\text{C}_{10}\text{H}_{42}\text{O}_{14}\text{N}_{12}\text{Co}_2$ requires Co = 17.55; NH_3 = 25.29; NO_3 = 18.45 per cent.).

All the salts in this section are sparingly soluble in cold water and are characterised by giving, with potassium chromate, a yellow precipitate which is both a nitrate and a chromate.

3. *Aquopentammine salts.* *Aquopentamminecobaltic nitrate succinate* [XI, with $\text{Y} = (\text{CO}_2)_2(\text{CH}_2)_2$] was obtained in a yield of 3.3 grams (Found: Co = 16.92; NH_3 = 24.91; NO_3 = 18.04. $\text{C}_4\text{H}_{21}\text{O}_8\text{N}_6\text{Co}$ requires Co = 17.34; NH_3 = 25.00; NO_3 = 18.24 per cent.).

Aquopentamminecobaltic nitrate tartrate [XI, with $\text{Y} = (\text{CO}_2)_2(\text{CH}\cdot\text{OH})_2$] separated as a brownish-red crust of minute crystals. Yield 3.5 grams (Found: Co = 15.59; NH_3 = 22.73; NO_3 = 16.91. $\text{C}_4\text{H}_{21}\text{O}_{10}\text{N}_6\text{Co}$ requires Co = 15.85; NH_3 = 22.85; NO_3 = 16.66 per cent.).

Aquopentamminecobaltic nitrate fumarate, $[\text{H}_2\text{O}\cdot\text{Co}(\text{NH}_3)_5]\text{Y}(\text{NO}_3)\cdot 2\text{H}_2\text{O}$, where $\text{Y} = \text{CO}_2\cdot\text{CH}\cdot\text{CH}\cdot\text{CO}_2$, was obtained in a yield of 2.7 grams (Found: Co = 16.01; NH_3 = 22.75; NO_3 = 16.82; H_2O = 9.44. $\text{C}_4\text{H}_{16}\text{O}_8\text{N}_6\text{Co}_2\cdot 2\text{H}_2\text{O}$ requires Co = 15.77; NH_3 = 22.73; NO_3 = 16.57; H_2O = 9.62 per cent.).

Aquopentamminecobaltic nitrate adipate (XI, where $\text{Y} = \text{CO}_2[\text{CH}_2]_4\cdot\text{CO}_2$) was obtained in a yield of 1.4 grams (Found: Co = 16.06; NH_3 = 23.21; NO_3 = 16.70. $\text{C}_6\text{H}_{25}\text{O}_8\text{N}_6\text{Co}$ requires Co = 16.02; NH_3 = 23.10; NO_3 = 16.85 per cent.).

Aquopentamminecobaltic nitrate methionate [XI, where $Y = (SO_3)_2CH_2$] was obtained in brownish-red, prismatic needles (Found: $Co = 14.37$; $NH_3 = 20.69$; $NO_3 = 14.98$. $CH_{19}O_{10}N_6S_2Co_2H_2O$ requires $Co = 14.65$; $NH_3 = 20.43$; $NO_3 = 14.90$ per cent.).

All the above salts are sparingly soluble in cold water and are converted by potassium chromate into chromatopentamminecobaltic nitrate.

Orthophosphatopentamminecobaltic dihydrogen orthophosphate (XIV) was obtained in small, reddish-brown, flat needles on the addition of 5 grams of the carbonato-nitrate to a solution of 3 grams of orthophosphoric acid in 25 c.c. of water at 40° . Yield 2.8 grams (Found: $Co = 15.91$; $NH_3 = 22.42$; $PO_4 = 50.98$; $H_2O = 9.72$. $[HPO_4 \cdot Co(NH_3)_5]H_2PO_4 \cdot 2H_2O$ requires $Co = 15.81$; $NH_3 = 22.79$; $PO_4 = 50.94$; $H_2O = 9.65$ per cent.). The salt is very sparingly soluble in cold water and readily soluble in dilute alkali or mineral acid solutions. The water of crystallisation is lost over sulphuric acid at the ordinary temperature. The salt melts at the temperature of the steam-oven.

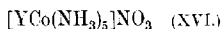
Citratotripentamminecobaltic dihydrogen citrate (XV) was obtained in minute pink crystals in almost quantitative yield when 5 grams of the carbonato-nitrate were added to a solution of 4 grams of citric acid in 40 c.c. of water at 50° . The solution was kept at 50° until effervescence ceased, and the salt separated quickly on cooling (Found: $Co = 9.52$; $NH_3 = 14.34$; $C_6H_5O_7 = 75.44$. $C_{42}H_{94}O_{49}N_{15}Co_3$ requires $Co = 9.99$; $NH_3 = 14.41$; $C_6H_5O_7 = 74.80$ per cent.). This salt is only sparingly soluble in warm water. It has an acid reaction and dissolves in sodium bicarbonate solution, but cannot be reprecipitated by acid. The constitution was further checked by titrating the salt with standard alkali solution [0.3471 gram required 23.2 c.c. of $N/10$ -barium hydroxide (theory 23.53 c.c.). 0.4751 Gram required 16.5 c.c. of $N/5$ -sodium hydroxide (theory 16.1 c.c.), using phenolphthalein as indicator].

Molecular Conductivities.

Since few chemical reactions are possible with the complex salts described in this paper owing to their sparingly soluble nature, the determination of their molecular conductivities has been found useful in checking the formulae suggested for them. The electrical conductivities were measured with the identical apparatus described in Part VII of this series (T., 1922, **121**, 453). All measurements were made at 25° and so far as possible all solutions were made at 5° and were freshly prepared for each stage of dilution. Owing to the moderate solubility of the salts and the need for obtaining a

solution quickly to avoid much hydrolysis, measurements have only been made for $v = 512$ and 1024 litres.

The results have been divided into five classes corresponding to the five classes of compounds already described. To simplify the table, the following five general formulæ are referred to:—XVI, V, VI, VII, XI.



A peculiar catalytic action has been discovered during the measurement of the electrical conductivities. It is most marked in the case of the salts represented by formula XVI. These salts show little or no hydrolysis of the complex in dilute solution even above 25° , until the solution is in contact with the platinum electrodes. Then hydrolysis at once begins, in some cases quickly, and aquo-salts are produced. The oxalato- and chromato-nitrates give reactions for oxalate and chromate after remaining in the electrolytic cell for one hour, whilst a solution outside the cell will show no such reaction even on the next day. The catalytic hydrolysis is apparently due to the platinum black on the electrodes and only occurs in the solution immediately surrounding these. It is not necessary to have any current passing for the effect to be produced. It may be that this unusual effect is connected with the presence of a "bound" ion in the structure of these salts (see formulæ I, II, III, IV), but further investigation is necessary on this point.

Whilst the catalytic hydrolysis is most marked in the foregoing class, it is also in evidence in the others except those containing the aquo-salts. It is evident that the electrodes can hasten hydrolysis of the complex in these series of salts. It is also noticeable in a less degree in a normal type of salt like nitratopentamminecobaltic nitrate.

Some aquo-salts show evidence of hydrolysis, particularly a succinate and a tartrate. This may be regarded as indicating that there is a tendency in these cases for the organic acid radicle to enter the complex.

The chromato- and carbonato-nitrates have been included in the first class, as no record of their conductivity could be found in the journals. Sulphatopentamminecobaltic nitrate is also included, since Werner and Miolati (*Z. physikal. Chem.*, 1896, 21, 235) record that, for $v = 512$ and 1024, $\mu = 94.64$ and 101.6, respectively, without any observation that hydrolysis occurred. This has been found to be unusually small in this case.

In order that the results may be more readily compared, τ represents the volume of solution containing one gram-atom of cobalt.

Y in formula XVI.	μ_A^*		μ_B^*		μ_C^*	
	$v=512.$	$v=1024.$	$v=512.$	$v=1024.$	$v=512.$	$v=1024.$
Carbonato-	136.4	143.4	136.4	143.4	189.3	254.9
Sulphato-	96.5	101.4	98.2	101.9	101.7	106.8
Chromato-	125.6	120.3	125.6	120.3	228.0	309.4
Oxalato-	136.4	148.5	136.4	148.5	173.2	204.7
Maleato-	145.4	148.7	145.4	148.7	156.4	159.7
Sulphoacetato- ...	128.1	120.6	131.4	122.6	141.3	151.2
Phthalato-	97.2	99.6	99.1	100.8	104.7	112.7
Mesotartarato- ...	212.9	241.4	210.5	241.4	247.4	328.7
Y in formula V.						
Malonato-	233.3	249.2	243.4	263.7	319.5	348.9
Maleato-	234.6	266.2	239.3	273.3	296.9	312.8
Malato-	255.7	267.8	255.7	267.8	324.1	343.7
Phthalato-	270.0	271.6	272.4	278.3	356.1	348.9
Citraconato-	245.5	252.0	254.3	272.5	267.5	278.0
Itaconato-	243.4	251.2	260.7	282.3	274.9	300.9
Glutarato-	256.4	256.5	268.7	273.6	298.5	325.4
Adipato-	254.9	257.1	267.8	283.5	331.1	348.9
Y in formula VI.						
Malonato-	240.6	260.7	242.9	266.9	259.5	300.4
Malato-	246.5	266.2	258.6	281.8	299.2	331.1
Citraconato-	270.1	267.9	272.4	270.1	275.3	273.3
Itaconato-	228.0	229.8	229.8	231.4	233.8	231.4
Glutarato-	235.1	241.3	247.9	257.7	283.5	316.1
Methionato-	273.3	282.7	276.0	287.8	287.1	295.6
Mesotartarato- ...	210.8	243.0	215.2	245.0	270.1	307.6
Y in formula XI.						
Succinate	250.0	271.6	251.2	274.1	260.7	292.7
Tartrate	260.5	300.4	269.5	303.4	304.1	331.8
Fumarate	239.7	250.3	239.7	250.3	239.7	250.3
Adipate	306.6	318.4	308.6	324.1	324.1	325.2
Methionate	274.6	297.5	274.6	297.5	274.6	297.5
Y in formula VII.						
Succinate	350.5	367.0	350.5	367.0	350.5	367.0
Tartrate	247.9	268.9	247.9	268.9	247.9	268.9
Fumarate	229.2	248.7	229.2	248.7	229.2	248.7
$\mu = 1024.$ 2048. 1024. 2048. 1024. 2048.						
Phosphato- pentammine- cobalt	143.9	133.7	147.4	137.1	180.1	214.1
Citratopentam- minecobalt ...		137.1		138.7		215.4

* μ_A represents the values for freshly-made solutions, μ_B the values for the same solutions, kept for one hour in the flask, and μ_C the values for the same solutions after contact with the electrodes for one hour without being disturbed in any way.

To the phosphato- and citrato-salts mentioned above have been given formulæ (XII and XIII) which indicate that they should be ion-electrolytes in solution, for the formation of ions is impossible unless hydrolysis occurs. If they are aquo-salts, the values of μ should exceed 300. It appears reasonable to suggest that

hydrolysis has occurred during solution, because the salts are very insoluble and heating to 50° was necessary to obtain the solution for $v = 1024$ in the case of the phosphato-salt and for $v = 2048$ in the case of the citrato-salt. The fact that the value of μ for $v = 2048$ is less than that for $v = 1024$ supports this conclusion in the case of the phosphato-salt. After the solution has been prepared, and the temperature maintained at 25° , hydrolysis proceeds but slowly until the platinum electrodes disturb the equilibrium; thereafter the rate of hydrolysis is accelerated as in the cases mentioned above. It was mentioned in the section on preparations that the phosphato-salt in solution gives a precipitate with silver nitrate; this result can be similarly explained as due to hydrolysis having occurred, whereby the phosphate radicle is removed from the complex.

The view that the behaviour of the foregoing substances in solution is due to hydrolysis is supported by the fact that the phosphato- and citrato-salts do not lose their water of crystallisation at 100° . It would seem that this water is firmly bound in the molecule in some way which enables the salt to change into an aquo-salt. It has been found that the crystals of both salts change on keeping, apparently into aquopentammine salts. The following figures were obtained four months after the values already given had been measured. For $v = 2048$, the phosphato-salt and the citrato-salt now gave $\mu = 214.1$ and 218 , respectively, these values remaining constant. These results support the suggested formulæ (XII and XIII) for the salts, when freshly prepared, and account for the conductivity values obtained.

The change which occurs on keeping the crystals of these salts is paralleled by the observation of Jørgensen (*J. pr. Chem.*, 1885, [ii], 31, 50) that crystals of aquopentamminecobaltic nitrate change at the ordinary temperature into nitratopentamminecobaltic nitrate after several months.

Addendum.

Additional experimental evidence is given below to show that the solution of aquopentamminecobaltic nitrate, prepared as described (p. 565), is different in chemical behaviour from an aqueous solution of pure aquopentamminecobaltic nitrate. It is suggested that the aquo-nitrate in solution can change into the nitratopentammine nitrate and that the presence of sodium nitrate facilitates this conversion. Measurement of the conductivities of solutions of pure aquo-nitrate support this view.

For $v = 256$, 512 , and 1024 , Werner and Miolati (*Z. physikal. Chem.*, 1896, 21, 237) give the values of μ as 344.6 , 362.3 , and 379.4 . If fresh solutions be made at each stage, the value of μ

will be found to decrease owing to the action of the electrodes. The present author thus obtained the following values:

For $v = 256$	$\mu = 351.1$	340.6 (after 1 hr.)	340.1 (after 2 hrs.)	
$= 512$	$\mu = 374.9$	360.0	359.0	"
$= 1024$	$\mu = 396.9$	380.0	378.0	"

The most probable explanation is that there has been conversion into nitratopentammine nitrate to a small degree. The change was found to occur slowly when the solution was not put into the Kohlrausch cell.

When trisodium phosphate was allowed to react with a solution of pure aquopentammine nitrate, minute, brick-red crystals were readily obtained which were identical with the phosphatopentamminecobalt already described. A similar salt was obtained from aquopentamminecobaltic chloride. Whilst the salt from the aquo-nitrate gave results for molecular conductivity identical with those already recorded for phosphatopentamminecobalt, the phosphate obtained from the aquo-chloride gave much higher figures, namely, for $v = 2048$, $\mu = 206.9$, and this became 211.2 after one hour in the cell, showing that this salt was at least in part aquopentamminecobaltic phosphate. This suggests that the aquo-nitrate changes more readily into the acido-salt than does the aquo-chloride.

Potassium citrate also was allowed to react with the aquopentammine nitrate and the chloride. Crystals were readily obtained which in each case were identical with those of the citratocompound already described. The molecular conductivities were higher, however: For $v = 2048$, the salt from the aquo-nitrate gave $\mu = 177.9$, and 215.4 after 1 hour in the cell, whilst the salt from the aquo-chloride gave $\mu = 244.1$, and 279.4 after 1 hour in the cell. All the foregoing results therefore show that the aquopentamminecobaltic nitrate solution used in this work had a specially reactive nature.

It has not so far been possible to obtain a series of chlorides or other salts corresponding to the nitrates described. The possibility of obtaining chlorides is still under investigation.

The author's thanks are due to Miss C. M. Butcher, B.Sc., for much valuable assistance during the preliminary stages of the work.

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[Received, December 21st, 1922.]

LXIX.—*Chloroiodoacetic Acid.*

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IODINE monochloride acts vigorously on $\alpha\beta$ -dichlorovinyl ethyl ether with evolution of heat. The solution becomes dark violet and iodine separates. If the ether is kept cool, and the monochloride is added very gradually, but little iodine is set free, and the mixture, on standing exposed to the air, emits a colourless, acrid, inflammable vapour containing ethyl chloride. At the same time crystals of chloroiodoacetic acid are formed on the sides of the containing vessel. The product of the action appears to be chloroiodoacetyl chloride,



which is converted into the acid by the absorption of water from the air. If air is excluded, and the mixture left for some time, the acid chloride is produced in good yield, and although it cannot be purified it can be used, in the crude form, for the preparation of the acid and its derivatives.

Chloroiodoacetic Acid.—Iodine monochloride (1 mol.) was added as above to $\alpha\beta$ -dichlorovinyl ethyl ether (1 mol.), and the mixture kept in a sealed vessel for three weeks. It was then heated at 50° to expel ethyl chloride and, after cooling, filtered through glass wool to remove solid iodine. Water (1 mol.) was added in small quantities at a time and the mixture left over-night. It solidified almost completely, the yield of crude chloroiodoacetic acid being 60 per cent. of the calculated. The acid was purified by crystallisation from light petroleum. Thus obtained, it forms colourless, lustrous leaflets melting at 90° (Found: Cl = 15.50, 15.32; I = 57.50, 57.15; equivalent = 217.9; $M = 223.7$. $\text{C}_2\text{H}_2\text{O}_2\text{ClI}$ requires Cl = 16.06; I = 57.54 per cent.; $M = 220.4$).

The acid is not perceptibly hygroscopic, although it dissolves readily in water and the ordinary organic solvents. When dry, it does not change on exposure to the air. But its solutions are very sensitive to light. Colourless solutions in light petroleum or benzene turn violet almost immediately when exposed to bright sunlight. The salts of the ordinary metals are all soluble in water. The barium salt could only be crystallised from very concentrated solution (Found: Ba = 24.19. $\text{C}_2\text{H}_2\text{O}_2\text{Cl}_2\text{I}_2\text{Ba}$ requires Ba = 23.84 per cent.).

Chloroiodoacetamide is formed on treating a solution of the crude chloroiodoacetyl chloride described above with dry ammonia. It crystallises from water or benzene in brilliant white needles melting

at 140° (Found: N = 6.51; Cl = 16.00; I = 57.20. Calc., N = 6.37; Cl = 16.19; I = 57.89 per cent.). It is evidently identical with the amide obtained by Willstätter and Hottenroth from impure ethyl chloriodoacetate and ammonia (*Ber.*, 1904, **37**, 1786).

Chloriodoacetanilide is similarly prepared by the action of aniline on the chloride in light petroleum solution. It crystallises from water or benzene in white needles melting at 142° (Found: N = 4.82; Cl = 11.93; I = 42.94. C_8H_7ONClI requires N = 4.74; Cl = 12.00; I = 42.98 per cent.).

Esters of chloriodoacetic acid can be obtained from the above chloride, or, in this case, if the alcohol is added to a freshly prepared mixture of dichlorovinyl ethyl ether and iodine monochloride, a violent reaction sets in on warming and the ester is formed. Liquid esters could not be isolated in a pure condition, but solid esters can be crystallised out and purified.

Phenyl chloriodoacetate crystallises from light petroleum in brilliant colourless leaflets melting at 110° (Found: Cl = 11.98; I = 42.78. $C_8H_6O_2ClI$ requires Cl = 11.97; I = 42.83 per cent.).

The replacement of a chlorine atom in phenyl dichloroacetate by a bromine atom has only a slight effect on melting point and crystalline form (Crompton and Triflitt, T., 1921, **119**, 1874). When the bromine is replaced by iodine, the melting point rises from 46.5° to 110° . Also, phenyl chlorobromoacetate and chloriodoacetate do not form mixed crystals. This is shown by the melting points of their mixtures:

Molecular percentage of chlorobromoacetate.	M. p.	Molecular percentage of chlorobromoacetate.	M. p.
100	46.5	62.2	75.7
90.0	42.8	50.0	87.5
88.2	42.0	37.1	96.0
82.0	42.6	28.0	102.5
80.0	47.9	7.5	107.6
78.8	52.0	0	110

These numbers give a melting point curve of the usual type, the eutectic mixture, containing 82.9 per cent. of the chlorobromoacetate, melting at 39.2° .

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(Received, February 5th, 1923.)

LXX.—*Interfacial Tension.*

By JAMES ROBERT POUND.

THE measurement of the interfacial tensions of liquids by the drop-weight and the capillary tube methods has been studied by Harkins and Humphrey (*J. Amer. Chem. Soc.*, 1916, **38**, 228, etc.) and by Reynolds (T., 1921, **119**, 460). Reynolds found that the drop-weight method gave, on the average, results that were 78·8 per cent., or roughly four-fifths, of those found by the capillary tube method. But this can be only an approximate relation, as the drop-weight method is affected by so many factors. By means of the capillary tube method Reynolds has obtained accurate results for the interfacial and the surface tensions of various mutually saturated liquids. He has proved that the former values are calculable from the latter, that is, the interfacial tension between two liquids, A and B, is the difference between the surface tension of A, saturated with B, and the surface tension of B, saturated with A, or $\gamma_{AB} = \gamma_A - \gamma_B$ (compare also Antonoff, *J. Russ. Phys. Chem. Soc.*, 1907, **39**, 342; *Phil. Mag.*, 1918, [vi], **36**, 377). For pure liquids, the interfacial and the surface tensions of which are constant at the one temperature, Reynolds has proved the above relation to hold within the limits of experimental error (*ca.* 1 in 200). The relation is true also for mixtures of organic liquids in contact with water when the interfaces are freshly formed, but here the interfacial tension in general diminishes with the age of the interface, because concentration of one or more components of the complex liquid will occur there and the interfacial tension tend to a minimum. However, even in such cases the law holds if the contemporaneous surface tensions and interfacial tension are known (see Reynolds's results for colloidal solutions). Surface concentration does not occur (or occurs quickly to a very slight extent) with some solutions; for example, benzene and aqueous solutions of salts, etc., give constant interfacial tensions that obey the normal law. Nevertheless, where γ_{AB} is much smaller than $(\gamma_A - \gamma_B)$ and varies with the age of the interface, it is certain that physical action (surface concentration) or chemical action has occurred; conversely, a normal value of γ_{AB} ($= \gamma_A - \gamma_B$) and its constancy are proof of the purity of the liquids used and of the absence of physical or chemical action at the interface. These results of Reynolds are substantiated by the present work.

The following determinations of interfacial tension were made in an apparatus practically the same as Reynolds's (*loc. cit.*). The capillary tube was placed centrally and vertically in a graduated

tube, which was fixed in a thermostat. The apparatus was thoroughly cleaned with chromic acid mixture, washed well, and filled with pure, air-free water; the second liquid was introduced from the top or the bottom according as it was lighter or heavier than water and allowed to enter the capillary.

The liquids being at rest, the positions of the interfaces are read off against the graduated tube, and the difference of level between the interface in the capillary tube and that in the outer tube is obtained in terms of the scale on the latter. Air-free water must be used, as if bubbles of air appear after the experiment is started they will probably enter the capillary and thus spoil the experiment; even if they form only in the outer space or annulus, they will disturb and deform the interface there, making its position difficult to read. The meniscus in the annulus should be horizontal, but a slight inclination therein may be readily allowed for when reading off its position on the scale; a slight inclination of the annular meniscus is due to the capillary tube not being set perfectly centrally in the wider tube or to the "oil" passing irregularly through the glass knobs that keep the capillary in position. In this arrangement errors due to parallax must be guarded against. The apparatus was always first wetted with water and then no difficulty was experienced in getting the "oil" to enter the capillary and to displace the water from the glass surfaces.

The apparatus was made in triplicate; two were used in a thermostat and the third was water-jacketed only. The former two were of similar dimensions: and one of them (apparatus 1) had the following dimensions and constants:

Value of one division of the scale on the outer tube = 0.5138 cm. = μ .

Internal radius of the capillary tube = 0.07722 cm. = r .

Rise of water in the capillary tube when in position in the graduated tube at 30° = 3.006 divisions = 1.5445 cm. = β .

Rise of water in the capillary tube when set in open vessel at 30° = 1.868 cm. = z .

Internal radius of the graduated tube = 0.787 cm.

External radius of the capillary tube = 0.4 cm.

Now r was determined by calibration with mercury, the capillary tube, before selection, being proved to have a uniform bore. μ was determined against a standard scale. β was found by direct estimation in the apparatus at 30° : the apparatus was filled with water, which was run out in stages, the position of the annular meniscus and that of the capillary tube meniscus being observed on the scale of the outer tube at each stage, so that from one setting of the apparatus the mean water rise for all positions in the capillary

tube was found, and several such experiments were carried out at different times, involving quite separate settings of the whole apparatus. Direct observation of this water rise in the apparatus by means of a micrometer microscope is inconvenient, and is no more accurate, since the position of the lower or annular meniscus is extremely difficult to locate by the microscope.

The water rise in the capillary tube, when set in an open vessel at the room temperature, was determined directly by the microscope, taking the mean of many positions throughout the length of the capillary. The open vessel used was of 4.6 cm. radius. The figure thus obtained corresponded well with that demanded by the usual theory, namely,

$$\gamma = \frac{1}{2}rg(\rho - \rho')(h + r/3) \quad \dots \quad (1)$$

where γ = surface tension of liquid-air, here water-air, in dynes per cm., r = radius of the capillary tube in cm., ρ = density of the liquid (grams/cm.), ρ' = density of the air, g = the value of gravity, and h = height of liquid rise in cm. to the lowest point of the meniscus; the term $(h + r/3)$ embodies the correction for the liquid in the meniscus. Some authorities give $h_m/3$ for this correction, where h_m = the height of the meniscus, but it was found that for water in our capillary tubes h_m does not differ appreciably from r . Thus, in one experiment, $r = 0.07722$, $g = 980$, $\rho = 0.99916$ (at 15°), $\rho' = 0.00116$, and $\gamma = 73.60$ (C.G.S. units), whence h (calc.) = 1.917 cm., whilst h (observed, mean value) = 1.921 cm.; this difference falls within the possible experimental error of our (I.T.) measurements. Hence it was considered unnecessary to measure directly the water rise in the capillary when the latter was set in an open vessel at 30° , and this figure, α , is obtained by calculation (as above), taking $\gamma_{30} = 71.34$ dynes/cm.

It will be noticed that α and β differ considerably. The importance of this was recognised and the figure given for β is the mean of at least three separate determinations; all the above constants of the apparatus are, at least, means of duplicates, and the experimental errors involved are (\pm) r , 7700, μ , 200, α , 500, and β , 500. The value of gravity at Ballarat, calculated by the usual formula, is more than 979.9 cm./sec.², so that the value 980 may be taken in our calculations.

Now the interfacial tension is given by the equation

$$\gamma = \frac{1}{2}gr\lambda\mu(h + r/3\mu)(d - d'),$$

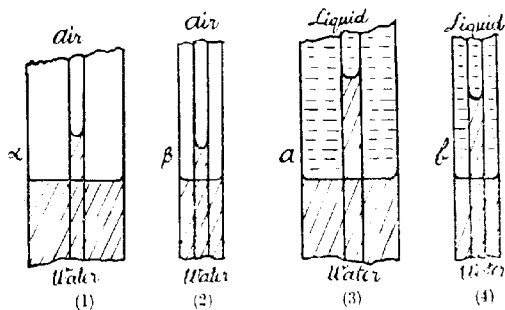
where γ = the interfacial tension in dynes per cm., g = value of gravity (C.G.S. units), r = radius of the capillary tube (cm.), λ = the ratio of the difference of level of the two liquids when the outer tube is of large diameter to that observed when the outer

tube is of small diameter (as in the apparatus), μ = the value of one scale-division of the apparatus in cm., h = the difference of level of the two interfaces (between the highest or lowest points of the menisci in and out of the capillary) in scale divisions, and d and d' = the densities of the two liquids.

This formula assumes that the angle of interfacial contact with the glass of the capillary tube is zero, a supposition which is supported by the appearance of the meniscus and by the investigations of Richards and Carver on surface tension determinations (see later). The critical factor in the equation is λ . What is the measure of the proportionality between the capillary rise (or fall) due to surface tension or interfacial tension when the capillary tube is set in a narrow tube and in a wide one? The measurement of surface tensions and of interfacial tensions by capillary tube methods is more dependent on the diameter of the larger vessel, in which the capillary tube is immersed, than is usually appreciated (see Richards and Coombs, *J. Amer. Chem. Soc.*, 1915, **37**, 1657; Richards and Carver, *ibid.*, 1921, **43**, 827; Rayleigh, *Proc. Roy. Soc.*, 1915, [A], **92**, 184).

It is probably correct to assume that there exists a constant ratio between the weights of liquids raised in the capillary tube when the latter is set first in an open or wide vessel and secondly in a narrow tube, whether in surface tension or interfacial tension measurements. These conditions are as follows :

FIG. 1.



For water-air systems (1) and (2), $w_a/w_b = (\alpha + r/3)/(\beta + r/3)$, where w_a and w_b are the weights of water raised in the two cases (wide and narrow tubes, respectively).

For liquid-liquid (or water-liquid) systems (3) and (4), $w_a/w_b = (a + r/3)/(b + r/3)$, by assumption, $(\alpha + r/3)/(\beta + r/3) = \alpha'/\beta'$, and thus $w_a = w_b(\alpha + r/3)/(\beta + r/3)$, where w_a and w_b are the

weights of liquid raised (or depressed) in the two cases (wide and narrow tubes, respectively).

Thus, in the interfacial tension measurement,

$$2\pi r\gamma = \frac{\alpha + r/3}{\beta + r/3}(b + r/3)(d - d')\pi r^2g,$$

$$\text{or} \quad \gamma = \frac{1}{2}gr\left(\frac{\alpha'}{\beta'}\right)\mu\left(h + \frac{r}{3\mu}\right)(d - d') \quad \dots \quad (2)$$

where $\alpha'/\beta' = \lambda$ (see above).

Thus $\gamma = k(d - d')(h + r/3\mu)$, where k is a constant for the one apparatus.

For the apparatus (1), referred to above,

$$\frac{\alpha'}{\beta'} = \frac{\alpha + r/3}{\beta + r/3} = \frac{1.868 + 0.0257}{1.5445 + 0.0257} = \frac{1.8937}{1.5702} = 1.206,$$

$$\text{and} \quad r/3\mu = \frac{0.07722}{3 \times 0.5138} = \frac{0.07722}{1.5414} = 0.050 \text{ (scale divisions)},$$

and the formula (2) becomes

$$\begin{aligned} \gamma &= \frac{1}{2} \times 980 \times 0.07722 \times 1.206 \times 0.5138 \times (h + 0.050)(d - d') \\ &= 23.45 \times (h + 0.050)(d - d'). \end{aligned}$$

Formula (2) was used in all our calculations of interfacial tension; for apparatus (2), $k = 20.83$ and $r/3\mu = 0.056$; for apparatus (3), $r = 0.0488$, $k = 1.096$, and $r/3\mu = 0.4$. Nevertheless it may be pointed out that α'/β' is nearly equal to α/β ; for example, for apparatus (1), $\alpha/\beta = 1.210$; and if h is not small, the term $r/3\mu$ may be omitted, and the formula

$$\gamma = \frac{1}{2}gr(\alpha/\beta)\mu h(d - d') = k'h(d - d') \quad \dots \quad (2')$$

may be used as a close approximation; for example, for apparatus (1), the equation (2') gives $\gamma = 23.53h(d - d')$, which, when h is greater than 5, gives results within less than 1 per cent. of those of equation (2).

In the densities given later, the fourth decimal place is exact and the fifth place, where given, is accurate to within two or three units.

This method affords an absolute measure of interfacial tensions and also a means of following the change of interfacial tension with time in those cases where this property depends on the age of the interface. The author has thus measured the interfacial tensions between purified liquids and water and also between commercial liquids, called oils, and water. Most of the work was carried out at 30°, but a few observations were made at other temperatures. For a pure liquid and water, the interfacial tension is constant, so that for each case only one figure need be quoted (Table I). For many of the commercial oils and water, the interfacial tension frequently varies greatly with the age of the interface; a set of values

TABLE I.
Interfacial tensions of pure liquids and water.

Liquid.	B. p.	d_4^{20} .	I.T. at 30° (dynes/cm.).
Benzene	80.0°	0.86707	32.50
Ether	34.6	0.7023	11.13
Chloroform	61.0	1.4688	31.41
Carbon tetrachloride.....	76.5	1.57426	42.75
Carbon disulphide	46.45	1.2477	46.31
Toluene	111.2	0.86604	34.6
Aniline	184.2	1.01298	6.00
Nitrobenzene	213.0	1.19219	24.1
Turpentine	160.6	0.85460	23.0
Paraldehyde	—	0.98193	9.60
Amyl alcohol (1)	131.1	0.8053	4.89
Amyl alcohol (2)	132.3	0.8036	4.83
Amyl acetate	140.7	0.8545	10.88
Ethyl acetate	77.0	0.88694	6.27
Cresol	206.0	1.02526	4.28
		d_4^{10} .	I.T. at 10°.
Benzene	—	0.8881	34.10
Ether	—	0.7247	10.19
Chloroform	—	1.5677	32.17

TABLE II.
Interfacial tensions of oils and water at 30°.

Oil.	Interfacial tension (dynes/cm.) after					Limit.
	d_4^{20} .	$\frac{1}{2}$ hr.	1 hr.	3 hrs.	18 hrs.	
Petrol	0.7078	44.2	44.2	44.2	44.2	43.1 (29 hrs.)
Kerosene (1)	0.7912	12.9	12.9	12.75	12.5	5.8 (12 days)
Kerosene (2)	0.7896	36.7	34.6	33.5	32.4	
Kerosene (3)	0.7887	46.2	46.2	45.5	45.1	43.2 (45 hrs.)
300-Test kerosene (1)	0.8380	39.95	39.55	39.5	39.4	37.5 (29 ")
300-Test kerosene (2)	0.8490	33.3	30.9	26.8	21.7	
Paraffin oil A	0.8688	26.8	23.2	19.8	—	13.5 (19 ")
Paraffin oil B (1)	0.8800	20.2	17.9	16.5	—	6.0 (27 ")
Paraffin oil B (2)	0.8786	25.9	20.4	17.7	—	8.8 (30 ")
Paraffin oil C	0.8972	35.3	33.8	32.3	—	26.5 (30 ")
B.P. Liquid Paraffin	0.8689	50.2	49.3	47.4	41.7	26.6 (11 days)
Eucalyptus (Cineol)	0.9119	15.65	15.4	15.4	15.1	
Eucalyptus (Phel- laudrene)	0.8493	17.75	18.2	—	—	18.7 (22 hrs.)
Turpentine	0.8615	6.68	6.68	6.68	—	7.12 (18 ")
Oleic acid	0.8855	12.80	12.80	12.80	12.80	12.15 (40 ")
Castor oil	0.9525	19.9*	19.7	19.0	18.2	16.9 (13 days)
Olive oil	0.9063	17.6	14.9	12.65	10.27	10.15 (22 hrs.)
Peanut oil	0.9074	14.75	13.9	12.75	11.2	10.8 (48 ")
Rape seed oil	0.9049	17.2	16.2	15.4	14.3	
Maize oil	0.9141	5.83	3.24	1.2	—	0.0 (8 ")
Linseed oil (raw) (1)	0.9338	4.41	4.34	—	—	
Linseed oil (raw) (2)	0.9213	7.8*	6.2	5.2	4.4	3.9 (48 ")
Linseed oil (boiled) ...	0.9375	9.57	9.10	8.51	7.42	6.9 (46 ")
Neatsfoot oil	0.9029	1.85	1.33	(40 minutes)		

* After $\frac{1}{2}$ hour.

for various times is given for each oil (Table II). The data were obtained in the following form. The time of making contact between

the second liquid and the water was noted, and after allowing the former five or ten minutes to attain the temperature of the thermostat it was slowly brought to rest at a first position in the apparatus so that the levels of the interfaces within and without the capillary could be read. The time of reaching this first position was noted; thereafter, as long as more water was not run or siphoned out of the apparatus, the level of the outer interface was constant, but that of the inner interface was in general not constant, the difference tending to diminish. For a pure liquid, the data would be as shown :

Interfacial tension of carbon disulphide-water at 30°. Apparatus 1.

First position reached ten minutes after contact.

Set.	Read- ing.	Time of reading after reaching position (mins.).	Levels of interfaces : within cap.	without cap.	Difference = h (scale divisions).	Mean.
1	1	6	94.33	86.58	7.75	7.75
	2	11	94.40	86.62	7.78	
	3	21	94.26	86.54	7.72	
	4	35	94.23	86.48	7.75	
2	5	8	87.02	79.20	7.82	7.83
	6	19	87.02	79.20	7.82	
	7	113	86.92	79.08	7.84	
and so on.						

It will be noticed that the times given for the readings in set 1 are taken from the time of reaching the first position and not from the time of contact. The first position is reached in from five to ten minutes after contact; but in this time the second liquid will scarcely have attained the temperature of the thermostat, and also if the second liquid is a viscous one it will lag behind in the capillary, and the time before equilibrium is reached will be correspondingly greater. In general, after setting the outer or annular meniscus in the first position, ten to fifteen minutes elapse before equilibrium is obtained in the capillary, and for viscous liquids such as the fatty oils a longer time is necessary. It will be seen in the case above quoted that after thirty-five minutes the position of the outer interface was changed, and after waiting for the capillary interface to reach a position of equilibrium a second set of readings was obtained. In this case five sets of readings were obtained from five positions at various points along the capillary tube, extending, in all, over four and a half hours. The mean of each set of readings was 7.75, 7.83, 7.85, 7.78, and 7.87, respectively; the general mean was $h = 7.82$, from which the interfacial tension was calculated as

46.53 dynes per cm. The mean of five similar sets of readings made in apparatus 2 gave $h = 8.72$, whence the calculated interfacial tension is 46.10 dynes per cm.; the value quoted in Table I is 46.31, the mean of the two experiments. The figures in Table I are the means of such duplicate experiments, one in apparatus 1 and one in apparatus 2, except for turpentine, amyl and ethyl acetates, and for the results at 10° . The differences between such duplicates varied between 1 per cent. and 0.1 per cent. of the interfacial tension value; on the whole, the interfacial tensions quoted are accurate to within ± 0.3 per cent.

For the commercial liquids (Table II) the time of a setting was usually several hours—in certain cases days, because here h and the interfacial tension decrease usually for hours. The data (selected) are given below for peanut oil–water.

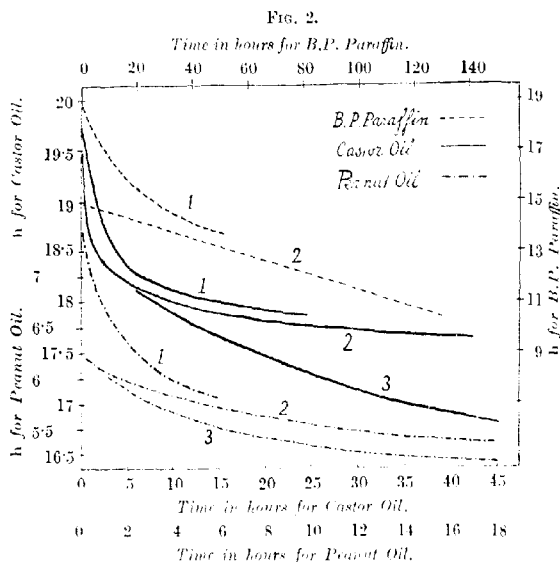
Interfacial tension of peanut oil–water at 30° . Apparatus 1.

First position reached eight minutes after contact.

Set.	Reading.	Time of reading after reaching position (mins.).	Levels of interfaces :		Difference = h .
			within cap.	without cap.	
1	1	10	49.48	56.68	7.20
	2	15	49.60	56.67	7.07
	3	20	49.73	56.68	6.95
	5	60	49.94	56.64	6.70
	7	210	50.59	56.62	6.03
2	8	14	52.42	58.60	6.18
	10	82	52.60	58.61	6.01
	11	109	52.63	58.60	5.97
	12	1180	53.22	58.60	5.38
3	13	13	59.17	65.39	6.22
	16	1500	60.21	65.37	5.16

It will be noticed that on changing the setting the interfacial tension or h increases, but never attains the first value; this is the usual behaviour—it is even exceptional that reading 13 should be higher than reading 8. From a graph showing the relation between h and t , the values of h were read after intervals of $\frac{1}{4}$ hour, 1 hour, 3 hours, and 18 hours from the time of the first setting. These values are given in Table II. In a few cases where the first setting was a short one, the figures for the 18-hour column are obtained from the second setting, treated as a continuation of the first. The figures in the last column (limit) of Table II generally refer to the last setting, probably the third or fourth of the series, and to the last reading of that setting; but where the last setting has been a short run or where other changes have occurred this limiting value

may not be actually the last reading. The change of interfacial tension with the age of the interface is shown in Fig. 2 in the cases of water with peanut oil, castor oil, and B.P. liquid paraffin; the numerals give the number of the setting—first, second, or third. In these cases of changing (decreasing) interfacial tension it will be seen that the rate of change is smaller the older the interface; in some cases, a limiting value of the interfacial tension is indicated. The change is, of course, due to alteration in the character of the interface as the result of (1) physical changes, that is, concentration



there of the components of the mixture that give the minimum interfacial tension, or (2) chemical changes, for example, the hydrolysis of the fatty oils. Such changes must be referred to individually, and as the nature of the material greatly influences the results obtained, it is desirable to indicate this with some completeness. The experiments recorded in Table II were not duplicated, except in the case of oleic acid, where the two experiments agreed closely.

The pure liquids referred to in Table I were all of the highest grade obtainable when purchased and were subsequently purified. Excepting the paraldehyde, they were all distilled, and a fraction-

ating column was used for all these liquids save for the aniline, nitrobenzene, and cresol. Details of each material are appended :

Benzene.—Commercial benzene was treated with concentrated sulphuric acid for nine days, washed with water, dried over calcium chloride, frozen (the residual liquid being rejected), melted, placed over sodium for twenty-four hours, and then distilled from sodium. The distillate collected boiled within 0.1° , the average boiling point (corr.) being 80.0° . Thorpe and Rodger give for benzene the b. p. 80.2° and a formula making d_4^{20} 0.8672 (*Phil. Trans.*, 1894, [A], 2, 185, 397). Parker and Thompson give for benzene d_4^{20} 0.8878 and d_4^{20} 0.86705 (T., 1922, 121, 1341). The interfacial tension was practically constant; in one of the experiments at 30° the value after four days was 1 per cent. less than the result quoted.

Ethyl Ether.—This ether had been purified some time previously by drying with calcium chloride, with phosphoric oxide for months, with sodium for four months, and distilling from phosphoric oxide, and was kept in the dark before the present use. It had b. p. 34.6° (corr.) and d_4^{15} 0.7195, whence are obtained the figures quoted (by Oudemans's coefficients of expansion). In the measurements of interfacial tension h is small and the meniscus is somewhat flatter than usual, so the quoted result may be a little high. Of course, ether and water are mutually soluble to some extent, which tends to make the menisci flatter and less sharp. The general rule is for the interfacial tension between two liquids to diminish with rise of temperature, and the exceptional result noticed in this case is explained by the varying solubility of ether and water with the temperature.

Chloroform.—The best commercial article was repeatedly washed with water, once with caustic soda solution, and again with water and was then dried over calcium chloride and fractionated. The distillate collected boiled at 61.0° (corr.); it had d_4^{20} 1.49734, whence, by Thorpe and Rodger's data, d_4^{20} 1.4688. The latter observers give b. p. 61.34° and d_4^{20} 1.4695, agreeing with Timmermans, Horst, and Onnes (*Compt. rend.*, 1922, 174, 365). From Herz and Rathmann's data (1913), d_4^{20} 1.4701. The interfacial tension was practically constant, the mean results being 31.40 and 31.41 dynes per cm. The chloroform becomes cloudy after an hour or so in the apparatus, but this change does not seem to be reflected in the value of the interfacial tension; after keeping with water for two months, a slight cloud is noticed at the interface and on disturbing the liquid the cloud sinks through the chloroform.

Carbon Tetrachloride.—The commercial material was treated with caustic soda solution, washed with water, dried with phosphoric oxide, and distilled. The distillate collected boiled within 0.1° ,

the average boiling point (corr.) being 76.5° . Thorpe and Rodger give b. p. 76.96° and d_4^{20} 1.57344, and Timmermans, Horst, and Onnes give b. p. 76.75° . Herz and Rathmann give d_4^{20} 1.5741, which is confirmed by Onnes's value at 0° . The interfacial tension was constant—in one experiment for more than twenty-four hours; the duplicate values were 42.62 and 42.88 dynes per cm., the mean of which is quoted.

Carbon Disulphide.—The commercial material was shaken with mercury and mercuric chloride at intervals during two days and filtered on to phosphoric oxide, from which it was afterwards distilled. The distillate collected came over within 0.08° , the average boiling point (corr.) being 46.45° . Its density, d_4^{20} , was found to be 1.27033, whence, by Thorpe and Rodger's coefficient of expansion, d_4^{20} 1.24774. These workers give b. p. 46.42° and d_4^{20} 1.24726; Onnes and his collaborators give b. p. 46.25° and, using Thorpe and Rodger's coefficient of expansion, d_4^{20} 1.2478. The interfacial tension was constant (see above).

Toluene.—The commercial material was shaken with phosphoric oxide and distilled therefrom after some hours. Two fractions were collected, the first boiling within 0.4° with the average b. p. (corr.) 111.0° , the second boiling within 0.3° with the average b. p. 111.3° . The first fraction had d_4^{20} 0.85612, the second had d_4^{20} 0.85596. The interfacial tension at 30° of the first toluene and water was found in apparatus 1 to be 34.80 dynes per cm., the mean value of 7 settings during six hours, during which the interfacial tension decreased slightly (about 1 per cent.); and the interfacial tension at 30° of the second toluene and water was found in apparatus 2 to be 34.40 dynes per cm., the mean of 7 settings of the same accuracy as before. In Table I, the mean density, boiling point, and interfacial tension of the two samples are recorded. If either or both samples are mixtures, the quoted interfacial tension is probably a little low, as a mixture in general has a lower value than its components. Timmermans, Horst, and Onnes give the b. p. of toluene as 110.7° and d_4^{20} 0.88445, whence, taking the coefficient of expansion as 0.00109 (Kaye and Laby's tables), d_4^{20} 0.8564.

Aniline.—Hopkins and Williams's "twice distilled aniline" was redistilled, and the pale yellow distillate collected came over within 0.5° , the average boiling point (corr.) being 184.2° . The b. p. of aniline is given as 184.36° (Knowles, *J. Ind. Eng. Chem.*, 1920, 12, 881), with a density at 15° that makes d_4^{20} 1.0136. The interfacial tension decreases slightly with time—by about 1 per cent. of the value in three hours in each setting, regaining this amount on resetting; the value recorded is the mean of the values obtaining to half an hour in all settings. After keeping with water for two

months, there was much cloud or white sediment at the interface; the aniline layer was then brown, but the dry aniline stock was only straw-yellow.

Nitrobenzene.—The commercial material was shaken with caustic soda solution and with water, dried over calcium chloride, and distilled. The bright yellow distillate collected came over within 1° , the average b. p. being 213.0° (corr.). The interfacial tension was constant for more than fifteen hours; but after the nitrobenzene had been in contact with the water for about three hours a white substance appeared in it at the interface—both in the annulus and in the capillary. The nitrobenzene became cloudy shortly afterwards. On keeping for two months in contact with water, the nitrobenzene remained yellow though cloudy, but that kept dry had become orange.

Turpentine.—The commercial material was an American turpentine, $[\alpha]_D^{20} + 0.1^\circ$. It was shaken with caustic soda solution and with water, and was dried with and distilled over calcium chloride. The distillate collected boiled from 159.6° to 161.6° ; it was slightly milky and was placed over calcium chloride for two days; it had then cleared, but had developed a slight yellow tinge; it was filtered off and used immediately. It now had $[\alpha]_D^{20} + 0.7^\circ$. In the first setting the interfacial tension was constant for more than one and a half hours at 23.0 dynes per cm., but thereafter it fell to the value 20.4 in seventeen hours. After the mixture had been kept for forty-five hours in the apparatus on the fifth setting, the interfacial tension had risen to 24.5 dynes per cm.; it subsequently fell to 23.0 after the mixture had been kept for sixty-five hours in all in the apparatus. The cause of this rise of interfacial tension with time is possibly oxidation (or hydrolysis?) of some components of the turpentine whereby the liquids at the interface are altered. The turpentine and the eucalyptus oils of Table II show a similar behaviour.

Paraldehyde.—The raw material was Morson's best B.P. paraldehyde; one-third of it was frozen out and the remainder poured off. (The freezing point of the original sample was about 10° .) The crystallised paraldehyde was melted and used. W. H. Perkin gives data indicating that his paraldehyde had d_4^{20} 0.98116 (T., 1884, 45, 470). The measurements of interfacial tension are complicated by the solubility of the paraldehyde in water (1 part in about 8 parts of water at 30°). The outer meniscus does not remain stationary, but rises; also, as the liquids dissolve one another, it is clear that $(d - d')$ must alter appreciably, since the difference of density is small to begin with. The value recorded may be taken as the maximum value, whilst for fresh surfaces the interfacial tension may be as low as 9.13 dynes per cm.

Amyl Alcohol.—The commercial material was placed over calcium chloride, which combined with the water and then with the alcohol, and some of the alcoholate dissolved in the liquid, making it more viscous. After two days the liquid was filtered hot and then fractionated. Two distillates were collected; the first came over within 1.3° , its average boiling point (corr.) being 131.1° , whilst the second distillate came over within 0.9° , its average boiling point being 132.2° ; during the distillation further calcium chloride separated out. The first sample had d_4^{20} 0.8053 and $[\alpha]_D^{20} -1.3^\circ$; the second sample had d_4^{20} 0.8036 and $[\alpha]_D^{20} -1.1^\circ$. Both samples were mixtures of several amyl alcohols, the main component being *isobutylcarbinol*, optically inactive or fermentation amyl alcohol. For the latter substance Perkin gives b. p. 131.5° and data indicating d_4^{20} 0.8014. The interfacial tension of sample 1 was practically constant during nineteen hours, the mean value of four settings being given. The interfacial tension of sample 2 decreased slowly, giving a value 10 per cent. lower than the recorded figure after eighteen hours; the first setting of one hour gave a constant interfacial tension, which is recorded. Both the recorded values may be somewhat lower than the interfacial tension of pure *isobutylcarbinol*.

Amyl Acetate.—The commercial material was washed with caustic soda solution and with water, dried over calcium chloride, filtered, and distilled. The distillate collected, a rather small fraction, boiled within 1.3° with average b. p. 140.7° (corr.); it had $[\alpha]_D^{20} +0.3^\circ$. It is probably mainly *isobutylcarbinyl acetate*. The interfacial tension was constant during three hours, the mean value being recorded; after twenty-one hours, the value was 10.77 dynes per cm. With this liquid, only one experiment was done.

Ethyl Acetate.—The commercial liquid was washed with sodium carbonate solution and with water, dried over calcium chloride, filtered off, and fractionated. Two fractions were collected; the first came over within 0.5° with average b. p. 76.6° (corr.); the second came over within 0.2° with average b. p. 77.0° (corr.). The first fraction had d_4^{20} 0.88567, and its interfacial tension was 5.84 dynes per cm.; the second fraction had d_4^{20} 0.88694, and its interfacial tension was 6.27 dynes per cm.; in both cases the value had decreased by about 3.5 per cent. after eighteen hours.

Perkin abandoned fractional distillation as a means of purification of ethyl acetate and synthesised it; he found for the pure liquid b. p. 77.5° and d_4^{20} 0.88818. Timmermans, Horst, and Onnes give b. p. 77.15° , and a density at 0° which, by Thorpe's coefficient of expansion, gives d_4^{20} 0.8885. It seems as if our sample of ethyl acetate contained alcohol (d_4^{20} 0.78075); but the second fraction was

almost certainly the purer and it gave the higher interfacial tension, which therefore is alone recorded in Table I.

Cresol.—The commercial material was a dark red liquid and was distilled slowly, a considerable amount of first distillate and of residue being neglected. The light yellow distillate collected came over within 3° , the mean b. p. being 206.0° (corr.) This is high compared with the b. p.'s of *o*-, *m*-, and *p*-cresols given by Campbell (I., 1922, 121, 850; 192° to 202°). His densities for *m*- and *p*-cresols are comparable with ours, his density for *o*-cresol being slightly higher. Our cresol is probably a mixture of the three isomerides together with some higher homologues. The interfacial tension increases with time; the figure recorded is the mean of the values of the first settings of the duplicate experiments, 4.41 and 4.15 dynes per cm., respectively, as the increase of interfacial tension is not appreciable for the first hour; after three hours there is an increase of about 10 per cent. in the value, and after eighteen hours an increase of about 20 per cent. This behaviour may be due to the solubility of the cresol in water, cresol on the average forming a $2\frac{1}{2}$ per cent. solution in water at 20° (Campbell, *loc. cit.*). It was noticed that the cresol in contact with water darkened in colour more rapidly than that kept dry in the stock bottle.

The liquids referred to in Table II were good commercial materials and were used as obtained. The first eleven liquids are products from American petroleum, that is, a Pennsylvanian or paraffin base crude oil, which was fractionated and refined by the Vacuum Oil Co.

The *Petrol* (motor fuel) was obtained (after refining, etc.) from that fraction of the crude petroleum boiling below 150° . The interfacial tension of this sample of petrol was constant during more than twenty-four hours and showed but a slight lowering after that time.

The *Kerosene* (illuminating oil) was the product obtained from the second distillate of the crude petroleum, namely, that boiling between 150° and 300° . The three samples of kerosene were of the same brand. *Kerosene* (1) was purchased locally. It showed a low interfacial tension compared with kerosenes (2) and (3), and after twenty-four hours the value diminished continuously, becoming less than half of the initial value after eleven days. Although obtained and used in good faith, it is certain that this sample contained some impurity (dissolved grease?) that gave it the low and decreasing interfacial tension. *Kerosene* (2) was a special sample obtained from the Vacuum Oil Co. *Kerosene* (3) was purchased locally, the sample being taken from a freshly opened 4-gallon tin with precautions to avoid contamination. Its interfacial tension decreased slowly. These three examples illustrate the differences

that may occur with different samples of one substance or product, especially when the property under investigation is, like interfacial tension with water, one that is markedly influenced by the presence of small amounts of impurity.

The third distillate, that boiling above 300°, of the crude petroleum yields on further distillation a high fire-test kerosene, and from the residue the various lubricating oils are obtained. 300-Test Kerosene is a kerosene with a flash-point about 300° Fahr. Two samples were given to the author by the Vacuum Oil Co. Sample (1) had the higher initial interfacial tension, and this decreased continuously save for temporary rises on fresh settings, as is usual; sample (2) had the lower initial interfacial tension, and this decreased more rapidly than that of (1). Sample (2) was very faintly yellow and slightly opalescent; sample (1) was light yellow and was filtered before use.

Paraffin Oils A, B, and C were lubricating oils presented by the Vacuum Oil Co. to the author, whose thanks are due, not only for these special petroleum products, but also for several fatty oils and for the following information (average values) supplied therewith.

Oil.	$d_{15.5}^{15.5}$	Viscosity at 40° (C.G.S. units).	Flash point (open Cleveland cup).
300-Test kerosene	0.858	0.0520	270° Fahr.
Paraffin oil A	0.865	0.116	340 ..
Paraffin oil B	0.890	0.212	405 ..
Paraffin oil C	0.908	0.446	435 ..

Paraffin Oil A was a lubricating oil for the lightest machinery; it was pale brown by transmitted light and greenish-yellow by reflected light (fluorescence or bloom); it had a slight odour like that of kerosene. Its interfacial tension changed rapidly at first, but more slowly after five hours.

Paraffin Oil B was a light-machinery lubricating oil. It was reddish-brown by transmitted light and greenish-blue by reflected light; its odour was very slight indeed. Two samples of this material were investigated; both gave decreasing interfacial tensions, but sample B(2) gave a higher value at the start.

Paraffin Oil C was a medium-machinery lubricating oil. It was red by transmitted light and greenish-red by reflected light and was practically odourless. Its interfacial tension decreased with time, but more slowly than those of the oils A and B; this may be due to the fact that the heavier petroleum products are closer fractions, containing the fewer individual paraffins.

B.P. Liquid Paraffin.—The British Pharmacopœia specifies a density of 0.860 to 0.890 at the ordinary temperature for this material, which is a colourless, viscous liquid, produced by treating

an oil like paraffin oil B with fuming sulphuric acid and subsequently filtering through Fuller's earth. Its interfacial tension decreased continuously over a long period; in the second and third settings (at least) the value after the first ten hours or so decreased linearly with the time (see figure).

Two typical samples of eucalyptus oil were used. The *Eucalyptus* (cineole) was given by John Macleod and Co. of Ballarat, whom the author has to thank also for the samples of castor and olive oils. This eucalyptus oil was pale yellow and was obtained from the southern Mallee. It was guaranteed to contain more than 80 per cent. of cineole (eucalyptol, $C_{10}H_{18}O$), the remainder being probably chiefly pinene and aromatic aldehydes. This oil had d_4^{20} 0.912 or d_4^{20} 0.924. Pure cineole is quoted as having d_4^{20} 0.929 and $[\alpha]_D^{20} + 1.1^\circ$; its surface tension at 13° is 29.6 dynes per cm. The interfacial tension decreased slowly with time in the first setting of eighteen hours; the next setting gave a slightly higher value, 16.0 dynes per cm. for the first five hours, after which the interfacial tension decreased slowly.

The *Eucalyptus* (phellandrene) was a faintly straw-coloured oil composed mainly of phellandrene, $C_{10}H_{16}$, and containing little or no cineole. It was obtained from *Eucalyptus dives* and was presented by W. K. Burnside and Co. of Melbourne. Phellandrene is quoted as having d_4^{20} 0.853. This oil had d_4^{20} 0.849 or d_4^{20} 0.861, and $[\alpha]_D^{20} - 13.6^\circ$; its surface tension at 13° was 28.75 dynes per cm. It gave with water an interfacial tension increasing with time. After it had been kept for twenty-two hours in the apparatus, the interfacial tension for the next setting of three hours was constant at 18.7 dynes per cm.

The *Turpentine* was bottled by Winsor and Newton, England; the bottle was well corked and sealed, but the sample may have been nine years old. It had a pale yellow tinge, and $[\alpha]_D^{20} + 12.6^\circ$, indicating that it was probably of Russian or Swedish origin. Its interfacial tension was constant for four settings, extending in all over five hours, after which time the value increased. This behaviour is similar to that of the purified turpentine and of the eucalyptus oils.

The *Oleic Acid* was a clear yellowish-brown liquid which was wholly solid at winter temperature (about 12°). It gave a practically constant interfacial tension for fifteen hours, showing if anything a slight increase from the initial value: thereafter the value diminished slightly.

The remaining samples were typical fatty oils. In these experiments on interfacial tension evidence was seen of the action of water on the oil. A turbidity developed in the oil in the apparatus

after a time, and a white material appeared at the outer meniscus and at the glass surfaces in contact with the oil, that is, at the outer wall of the capillary tube and the inner surface of the graduated tube above the annular interface. Presumably a film of water was left between the oil and the glass when the oil was run down into position. Hydrolysis of the fatty oils of course gives the fatty acids and glycerol; the turbidity may have been due to both of these and in addition the glycerol may have passed into the water at the interface. These changes in the nature of the interface were reflected in the lowering of the interfacial tension, although the initial lowering may be accounted for by the complex nature of these materials and the concentration of the components of lowest interfacial tension at the interface. In two experiments (those with neatsfoot and maize oil) the interfacial tension fell practically to zero after a few hours. In many cases the experiment had to be stopped because the turbidity was such as to make further readings impossible. The time interval in hours before turbidity appeared in an oil in contact with water at 30° was roughly as follows: for maize oil $\frac{1}{4}$, neatsfoot $\frac{1}{3}$, raw linseed $\frac{1}{2}$, olive 3, peanut 5, rape seed 6, boiled linseed 6, and castor oil 300. These times bear no simple relation to the common characters of the oils such as their iodine value or acid value.

The *Castor Oil* was of English manufacture or refining and was cold-drawn oil of finest medicinal quality. The interfacial tension decreased with time in the usual way, but not rapidly; the initial value recorded may be somewhat high, for the oil, on account of its great viscosity, lagged behind in the capillary tube and even after half an hour may have been above the equilibrium position. During the later stages of the later settings the interfacial tension decreased very slowly, seeming to reach a limiting value. No turbidity was noticed in the oil or at the interface even after fourteen days.

The *Olive Oil* was a sample of the best Spanish olive oil. The interfacial tension decreased with time. The figures recorded refer to the first setting, in which the lowest value was reached; the third setting gave after one hour the value 14.5 dynes per cm., and after forty-nine hours 10.3 dynes per cm., but the oil had then been turbid for a long time. This means that the contaminated surfaces had lower initial interfacial tensions and a slower rate of change than the fresh surfaces, but the latter may have been due to mechanical restriction of movement only.

The *Peanut Oil*, also known as earth-nut or arachis oil, was semi-solid at 10°; it was melted and filtered before use, giving a clear lemon-yellow liquid with nutty odour. Its interfacial tension data have been given at length above.

The *Rape-seed Oil* was clear and orange-coloured—a shade lighter than the maize oil.

The *Maize Oil* was orange-coloured, with a slight green fluorescence; it was slightly opalescent and smelt like castor oil. After contact with water, the oil lost its reddish-brown tint and became yellowish-brown. It developed turbidity with the water very rapidly and its interfacial tension decreased almost to zero within eight hours, the annular meniscus becoming flat and covered with the white deposit and then crinkling and moving as a skin.

The *Raw Linseed Oil* (1) was a sample bottled by Winsor and Newton, England. It was a perfectly clear, light yellow oil and very fluid. It also developed turbidity with great rapidity in contact with the water. The interfacial tension in the first setting of one hour decreased as shown in Table II; on re-setting, the value after a quarter of an hour was 5.3 dynes per cm., from which it fell to its initial (set 1) value in nineteen hours. The second-set figures are not shown in the table, as they refer evidently to self-contaminated surfaces (compare olive oil).

The *Raw Linseed Oil* (2) was a sample drawn from a cask obtained from Blundell, England. It was clear yellow and slightly opalescent. The initial interfacial tensions recorded may be too high, as a narrow capillary tube was used (only) in this experiment.

The *Boiled Linseed Oil*, Blundell's, was somewhat reddish-brown.

The *Neatsfoot Oil* was melted and filtered hot, when it formed a clear brown liquid. It was rapidly changed by contact with water, and its initial low interfacial tension rapidly decreased and after forty minutes the oil became so turbid that the experiment had to be stopped.

Table III gives the surface tensions of certain commercial liquids, and their initial interfacial tensions with water at various temperatures. In this table, where "saturated" (sat. or s.) follows the name of the oil, the latter was shaken with water beforehand, and the determinations were carried out on the oil so saturated with water and on the water so saturated with the oil; where "fresh" follows the name of the oil, the determinations were carried out on the commercial oil as supplied, and the figures for the water refer to distilled water. The figures in brackets are not determinations, but standard values taken from the usual sources. The interfacial tensions refer to a short time, not more than half an hour, after setting in the apparatus 3. Table III shows that the interfacial tensions between these liquids and water are considerably smaller than the difference between the surface tensions of the mutually saturated liquids or of the fresh liquids. Also the interfacial tensions are smaller than those between the purified liquids

TABLE III.

Interfacial tensions of oils, etc.

Oil (fresh, or saturated with water).	Temp.	Density (t_4) of oil,	I.T.	Density (t_4) of water,	Surface tension of oil,	Surface tension of water,
		f. or s.	dynes/cm.	f. or s.	f. or s.	f. or s.
(1) Benzene (sat.) ...	11°	0.8851	22.5	—	—	—
(2) Benzene (fr.) ...	18	0.8783	33.3	(0.9986)	28.9	(73.1)
(3) Carbon tetrachloride (sat.)	13	1.6084	42.7	1.0001	28.0	73.8
(4) Turpentine (sat.)	12	0.8707	15.0	0.9997	28.2	62.1
(5) Kerosene (sat.)	12	0.8039	19.8	0.9998	26.9	70.7
(6) Kerosene (sat.)	15	0.8020	19.0	0.9995	26.8	71.7
(7) Kerosene (fr.)	13	0.8035	15.9	(0.9994)	28.9	(73.9)
(8) Toluene (fr.) ...	25	0.8600	31.7	—	28.4	(72.1)
(9) Olive oil (fr.) ...	22	0.9114	19.7	—	(33)	(72.5)

Note: The surface tension of fresh (that is, dry) carbon tetrachloride at 13° = 28.0 dynes/cm., and of fresh turpentine at 12° = 29.2 dynes/cm.

In the above table the figures on each horizontal line refer entirely to either the fresh liquids or the mutually saturated liquids as stated.

and water. For example, from Table I, the interfacial tension at 25° of toluene-water would be 34.9 dynes per cm. (using the benzene-water interfacial tension temperature coefficient; see below); in Table III is given the value 31.7. This toluene was the parent of the pure sample of Table I and was itself fairly pure. The benzene (2) of Table III was apparently a good commercial sample; its interfacial tension was remarkably high. Harkins and Humphrey (*loc. cit.*) give for the interfacial tension of benzene-water the formula $\gamma = 35.54 - 0.056t$; this gives $\gamma_{30} = 33.86$, $\gamma_{13} = 34.53$, and $\gamma_{10} = 34.98$ dynes per cm. Our values for purified benzene are lower than these. The benzene (1) of Table III was a different sample of commercial benzene, and the saturated solutions used here were six weeks old. The turpentine of Table III was the parent of that of Table I. The kerosene of Table III was the kerosene (1) of Table II, and experiment (7) of Table III compares directly with that in Table II. Experiment (6) differs from (5) in that the saturated solutions were filtered before use in the former experiment, which was made a fortnight later than (5). The interfacial tension result in (7) is lower than those in (5) and (6) because impurities, concentrating at the interface, directly affect the former, whilst they are removed or remain behind in the separating funnel and cannot affect the latter. The olive oil in Table III is the same as that in Table II; the interfacial tension at 22° falls rapidly from the figure recorded.

In the case of the pure liquids and water (Table I), the liquids that are appreciably soluble in water tend to give low interfacial tensions in contact therewith, or there is a general correspondence

between the mutual solubility and the interfacial tension of two liquids. Both phenomena are largely influenced by mutually attracting groups in the molecules of the two liquids concerned; this view is a combination of the ideas of Young and of Langmuir. Thus the behaviour of benzene, toluene, carbon tetrachloride, chloroform, and carbon disulphide, and even of petrol and kerosene, may be contrasted with that of aniline, ether, amyl alcohol, and cresol. The former are saturated compounds or at least self-satisfied (as benzene) or, as it may be put, not prone to exercise secondary valencies; they are slightly soluble in water and vice versa, and their interfacial tensions with water are high. On the other hand, aniline and the oxygen compounds are potentially unsaturated and tend to exercise further valencies; they are appreciably soluble in water and vice versa, and their interfacial tensions with water are low. The interfacial tension between two liquids, A and B, is given by $\gamma_{AB} = \gamma_A - \gamma_B$ (see p. 578). If A stands for water, which has the highest surface tension of ordinary liquids, then a low interfacial tension between another liquid, B, and water must be due to the aqueous solution A' having a lower surface tension than that of water or to the solution, B', of water in the liquid B having a higher surface tension than that of the pure liquid B; that is, γ_A must be less than γ_A , whilst γ_B must be greater than γ_B , or both causes must operate. Now, when water dissolves in an organic liquid, the increase of surface tension is small. In Reynolds's results (*loc. cit.*) at about 18°, only two instances of such a rise of surface tension occur, namely, with benzene (0.4) and with aniline (0.3 dynes per cm.); with carbon tetrachloride, petrol, and turpentine, on saturation with water, there is no change of surface tension, and with his other liquids there is a slight fall of 0.1 to 3 dynes per cm.—on the average, 0.7 (compare Table III). But the lowering of the surface tension of water by the dissolution of even a small amount of an organic liquid in it may be large, for example, at 18° the surface tension of water is 73 dynes per cm., but on saturation with benzene the surface tension, according to Reynolds, becomes 63, with aniline 46, with ether 28, and with amyl alcohol 26 dynes per cm. The last two figures are the lowest recorded for such aqueous solutions by Reynolds (compare Table III). This fall of surface tension is roughly proportional to the amount of the organic liquid that dissolves in the water. Hence a low interfacial tension is determined more by the solubility of the organic liquid in the water than by that of water in the organic liquid: for example, compare carbon disulphide and chloroform—the latter is the more soluble in water and hence gives the lower interfacial tension with water, but water is more soluble in carbon disulphide than in chloroform. However,

the solubilities of partly miscible liquids generally rise and fall together, that is, if the solubility of A in B is large, then that of B in A is large also. In conclusion, then, the interfacial tension between two liquids, which equals the difference between the surface tensions of the mutually saturated liquids, is always the less the greater their mutual solubility; and when the mutual solubility is marked, the interfacial tension is much less than the difference of surface tensions of the pure liquids. The former is dependent on certain causes, to which also is due (at least in part) the mutual solubility of the liquids, but the interfacial tension depends as well on physical and chemical changes at the interface—changes of a different order from solution changes, although the underlying causes may be the same. The molecules of one liquid may be able to arrange themselves economically (that is, in a system of minimum potential energy) with those of a second liquid at an interface, without being able to intermingle freely with the latter; the former may be able to accommodate themselves to the latter at an interface (of approximately two dimensions) but not in a volume (that is, in three dimensions).

With the paraffin oils of Table II the interfacial tension is sometimes high, which probably is the normal behaviour of a pure paraffin (single substance) insoluble in water (compare Harkins, *loc. cit.*, who gives the interfacial tension of hexane–water as 49.5 dynes per cm. at 25°). The low interfacial tensions of most of these paraffin oils are probably due to their being complex mixtures and to the physical concentration at the interface of the components of lowest interfacial tension, or to the arrangement of the molecules at the interface in the configuration of least interfacial energy. Such a configuration is to be considered as a dynamic system and not as a static condition of the molecules. In this case a small amount of an impurity may well make a considerable difference in the system or in its stability and hence in the variation and diminution of the interfacial tension with time. It is well known that a mixture has this accommodating power of surface energy, for example, soap films, and stable froths on solutions. The eucalyptus oils and turpentine are appreciably soluble in water and therefore their interfacial tensions are low. In the case of the fatty oils, the low interfacial tension must be ascribed in the first place to their being complex mixtures and in the second place to their hydrolysis with water. No data could be found on the rate of saponification of the fatty oils with water at low temperatures. Lewkowitsch, in experiments on the hydrolysis of fats and oils by dilute acids at the boiling point, points out that castor oil is very slowly acted on compared with rape and other oils, and also that rapid saponification is usually, if

not always, dependent on emulsification, indicating that at the interface between the oil and the water saponification is rapid. That chemical action is rapid at the boundary of two phases is now well recognised, the catalytic action of surfaces being due to interfacial concentration, condensation, or absorption, all of which are related to changes in interfacial energy. Certainly the oils that the soonest gave evidence of hydrolysis at the interface were those of the lowest and of the most rapidly diminishing interfacial tension.

Summary.

The interfacial tensions of pure liquids in contact with water are constant at one temperature. The author's values are in general agreement with previous determinations. The interfacial tension between two liquids is the less the greater their mutual solubility.

The interfacial tensions of commercial liquids or oils in contact with water usually vary with the age of the interface; they nearly always decrease with time. In these cases the interfacial tensions are less than the difference of the surface tensions of the saturated liquids. The diminution of interfacial tension with time is pronounced even when chemical action between the liquids is improbable, for example, with paraffinic oils and water. It may be concluded that a mixture (of oils) will always give a variable interfacial tension with water due to physical concentration at the interface of the components giving the lowest interfacial tension. Further, when chemical change occurs at the interface, the tension will alter; in particular the fatty oils suffer hydrolysis in contact with water, and the resulting changes at the interface help in the lowering of the interfacial tension. The rate of lowering of interfacial tension frequently becomes slower as the interface ages; however, it can scarcely be said that there is any inferior limit to interfacial tension but zero.

In conclusion, the author desires to thank those firms who kindly gave samples of oils, especially the Vacuum Oil Co. of Melbourne.

THE SCHOOL OF MINES,
BALLARAT, VICTORIA.

[Received, December 28th, 1922.]

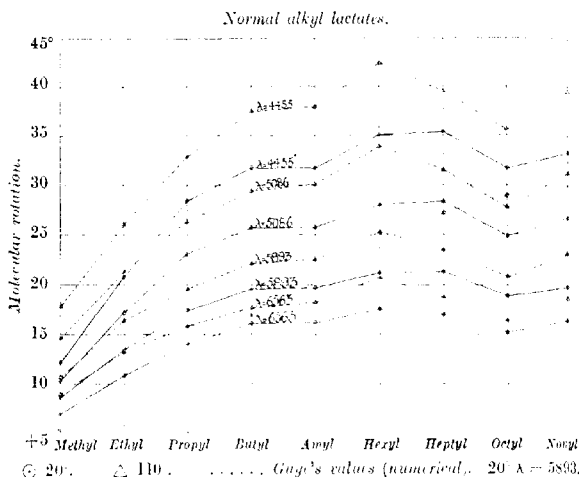
LXXI.—*Rotatory Dispersion of the Esters of Lactic Acid. Part I. Normal Esters.*

By CHARLES EDMUND WOOD, JOHN EDWARD SUCH, and FRANK SCARF.

THIS investigation deals with the normal alkyl *l*-lactates from the methyl to the nonyl ester inclusive.

The esters of lactic acid have been the subject of many investigations, notably by Purdie and Walker (T., 1892, **61**, 754; 1893,

FIG. 1.



use of morphine than by the older method of the fractional crystallisation of the zinc ammonium salts. In the work now described, the rotatory power of the *n*-propyl and *n*-butyl esters was higher, and the rotations of the *n*-heptyl and *n*-octyl esters were lower, than the calculated values obtained by Guye. With regard to the last two esters, no mention is made by the above authors of the source or boiling points of the respective alcohols employed; moreover, the low boiling point of the octyl ester would appear to indicate the presence of branched-chain compounds in their ester.

A further point of interest is that Guye obtained dispersion ratios by means of light filters of different solutions.

The various other workers who have prepared the methyl and ethyl derivatives are referred to in the experimental section, where their results are compared with the values obtained by us.

Molecular rotatory power of different esters for certain wave-lengths (Fig. 1).

Alkyl	λ	$[M]_D^{20}$				$[M]_D^{10}$			
		6563.	5893.	5086.	4455.	6563.	5893.	5086.	4455.
Lactate.									
Methyl	$\pm 6.97^\circ$	8.59 ²	10.68 ²	12.18 ²	8.89 ²	11.26 ²	14.70 ²	17.84 ²	
Ethyl.....	10.85	13.37	17.13	20.72	13.28	16.47	21.40	26.05	
<i>n</i> -Propyl ...	14.05	17.44	23.02	28.37	15.89	19.56	26.38	32.81	
<i>n</i> -Butyl ...	16.06	19.58	25.72	31.76	17.65	22.05	29.39	37.45	
<i>n</i> -Amyl ...	16.17	20.16	26.68	33.07	18.24	22.51	30.08	38.00	
<i>n</i> -Hexyl ...	17.53	21.25	28.03	35.10	20.71	25.40	34.00	42.45	
<i>n</i> -Heptyl ...	17.00	21.33	28.41	35.48	18.73	23.54	31.62	39.63	
<i>n</i> -Octyl ...	15.24	18.91	24.90	31.72	16.50	20.83	27.88	36.77	
<i>n</i> -Nonyl ...	16.40	19.85	26.80	33.50	18.80	23.27	31.40	39.75	

The series of normal esters gives molecular rotations which lie on a depressed curve for each of the above wave-lengths for the two temperatures recorded. The curves become more divergent as the molecular weight increases up to the hexyl or heptyl ester, and then tend to become parallel towards the nonyl ester. They all pass through a maximum value which persists (as far as our experiments show) at the hexyl ester, except for the lower temperature, in which case the molecular rotation increases slightly on passing from the hexyl to the heptyl member, for wave-lengths up to 5893 A.U. The maxima become more pronounced at higher temperatures and on passing from the red to the blue end of the spectrum.

It is possible that exaltation in rotatory power may be produced by a chain of five atoms returning upon itself, even when one carbon atom is replaced by oxygen. This may explain the maximum occurring at the hexyl ester, which contains a chain of ten atoms. No conclusion may be drawn in this way concerning the methyl ester, a five-atom chain compound, as it is the first member of the series. The similarity in the properties of the methyl and the

amyl ester is dealt with in the experimental section; the abnormality in their behaviour may be due to the fact that they terminate at approximately corresponding points on the helical carbon chain.

Guye gives the following table of molecular rotations :

	Propyl <i>d</i> -lactate.	<i>n</i> -Butyl <i>l</i> -lactate.	Heptyl <i>d</i> -lactate.	Octyl <i>d</i> -lactate.
$[M]_D^{25}$	-15.9° ($t^\circ=18$)	$+17.0^\circ$ ($t^\circ=17$)	-27.2° ($t^\circ=20$)	-28.9° ($t^\circ=18$)

All these figures are the result of calculations based on the percentage of water of crystallisation in the active materials employed, to correct for partial inactivity, and it is clear that they are open to criticism. These values (Fig. 1) lie on a broken curve, from which it is scarcely possible to predict, as Guye did, that "The values for the molecular rotations of the homologous lactic esters tend to a limiting value in the neighbourhood of the octyl ester." In all probability the reason for the rapid increase from the numerical value 17.0° for the *n*-butyl ester to the numerical value 27.2° for the *n*-heptyl ester, as well as for the high values obtained for the heptyl and octyl esters, respectively, lies in the fact that a small quantity of anhydride, or lactide, having a high rotation, was present: repeated fractional vacuum distillation of the small volumes of esters (3–5 c.c.) used by the above author must have been exceedingly difficult. The curves obtained by us are of a more continuous nature and show distinct maxima at the hexyl ester.

The Effect of Temperature on the Rotation.

The effect of temperature on the rotatory power of the individual esters is small. The rotatory power generally increases with temperature, the more rapidly the smaller the wave-length.

The esters form a series reaching maximum specific rotation at the butyl ester, thence decreasing in natural order to the nonyl ester, but the maximum molecular rotation occurs at the hexyl ester. Increase of temperature appears to affect the rotatory power of the lower esters more than that of the higher members. The curves for methyl lactate are practically straight lines, the curvature of which is only noticeable when drawn on a large scale. The curves for the remaining esters are flat, and maxima are shown by the butyl and octyl esters for certain wave-lengths. These maxima are displaced, in a similar way to the temperature-rotation maxima of ethyl tartrate, to the higher temperature with decrease in wave-length. Difficulty was experienced in taking readings at high temperatures on account of the esters evaporating so quickly in the neighbourhood of their boiling points that before constant tem-

perature was attained, loss of the ester rendered observation of rotation impossible.

The movement of the maxima for the two esters mentioned is given in the following table, this movement being approximately linear.

<i>n</i> -Butyl lactate.	λ .	<i>n</i> -Octyl lactate.
Maxima occur at		Maxima occur at
113—115°	6708	108°
116	6563	114
117	6438	120
120	5893	
121	5590	

In the case of the amyl and heptyl esters, the maxima are displaced, for the range of temperature considered, to a higher wave-length in the red; both esters, however, are approaching maxima, as is shown by the flatness of the curves.

It may be mentioned here that a number of intersections (maxima in temperature-rotation curves) occur between the rotation (1-dm.)-wave-length curves for different temperatures which disappear in the specific rotation-wave-length curves.

Rotatory Dispersion.

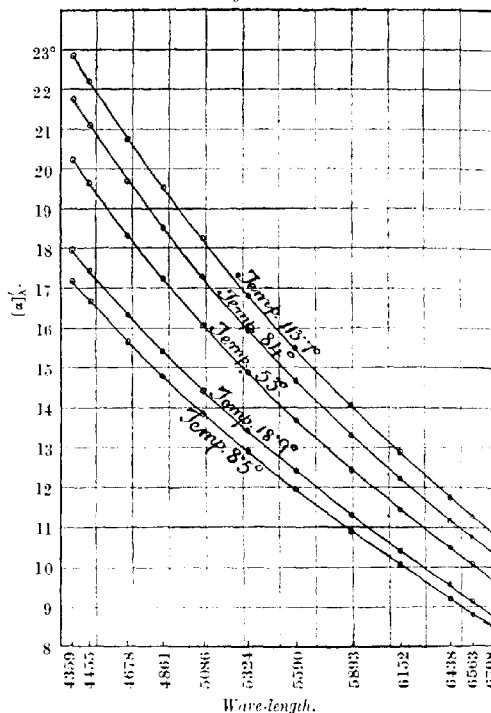
The rotatory dispersion curves for the ethyl ester given in Fig. 2 are typical of all the esters here described. In the case of the ethyl ester (similar to those of the methyl, propyl, amyl, hexyl, heptyl, and nonyl compounds), increase of temperature causes increase in rotation throughout the range of temperature considered, but in the case of the butyl ester (similar to that of the octyl compound) the dispersion curve for 126.1° lies below that for 104.5°, crosses it at λ 5590 Å.U., and proceeds to the blue end of the spectrum, thus indicating maxima for all wave-lengths greater than λ 5590 Å.U. in the temperature-rotation curves.

The rotatory dispersion exhibited by all the esters is of the same type, namely, normal and complex.

The points obtained by applying the usual test for complexity—plotting the reciprocal of the specific rotation against the square of the wave-length—do not lie on a straight line. If the curves be drawn for three different temperatures, namely, 20°, 60°, and 100°, it will be seen that a difference in sensitiveness to temperature is indicated between the ethyl and butyl esters by the increased proximity of the curves. For each individual ester rise of temperature causes slightly less curvature of the dispersion curves, but they are far from straight lines. It is of interest that such a simple series of esters, each member containing only one asymmetric carbon atom, exhibits complex rotatory dispersion. This complexity

may be due to (1) the persistently low rotation of the esters * (compare Frankland and Garner, T., 1919, 115, 636, who state that, with respect to anomalous rotatory dispersion, "the further the

FIG. 2.
Ethyl lactate.



* From the form of the curve $\alpha = c(\lambda^2 - \lambda_0^2)$, according as the constants c and λ_0 are real, positive, negative or imaginary, it can be shown that in no case can the above relation give a curve (α plotted against λ) which cuts the axis, unless $c = 0$; the curve then becomes the three straight lines $\alpha(\lambda^2 - \lambda_0^2) = 0$. Accordingly we should expect the above relationship, employed as a criterion of simplicity, to break down when it is applied to substances which give curves crossing the zero axis of rotation (plotting α against λ) or which would cross it if the experimental field were realisable.

It is therefore reasonable to suppose that the nearer the curves (α against λ) approach the zero axis, that is, the smaller the rotation of the substance, the less likely is it that the above test will show the substance to be simple with regard to optical rotatory dispersion.

rotation is removed from the zero line, by raising the temperature, the more simple (or less complex) does the rotation become," (2) the influence of the hydroxyl group attached to the asymmetric carbon atom.

Dispersion Ratios.

Temperature 20°.

Alkyl <i>l</i> -lactate.	λ 6708.	λ 5893.	λ 5461.	λ 5086.	λ 4359.
Methyl	0.683	0.883	1	1.102	1.280
Ethyl	0.680	0.873	"	1.119	1.302
Propyl	0.671	0.868	"	1.144	1.461
Butyl	0.674	0.868	"	1.136	1.445
Amyl	0.663	0.862	"	1.142	1.461
Hexyl	0.686	0.864	"	1.139	1.472
Heptyl	0.666	0.861	"	1.146	1.472
Octyl	0.673	0.863	"	1.142	1.496
Nonyl	0.679	0.854	"	1.153	1.486

Temperature 110°.

Methyl	0.647	0.869	1	1.132	1.375
Ethyl	0.671	0.869	"	1.130	1.413
Propyl	0.670	0.851	"	1.156	1.491
Butyl	0.657	0.856	"	1.138	1.501
Amyl	0.661	0.853	"	1.137	1.481
Hexyl	0.676	0.864	"	1.156	1.490
Heptyl	0.652	0.859	"	1.148	1.495
Octyl	0.650	0.859	"	1.147	1.570
Nonyl	0.659	0.852	"	1.150	1.513

The dispersion ratios for the series given in the above table show, with slight exceptions in the cases of the octyl and hexyl esters at 110°, which might be due to experimental error, that the value of the ratios for the wave-lengths given tends to become sensibly constant after the amyl member has been reached. Thus the substitution of one alkyl radicle for another in this series has apparently little effect on the value of the dispersion ratios.

The points on the characteristic diagram representing the rotations of *n*-octyl *l*-lactate at the higher temperatures do not fall on straight lines for the respective wave-lengths. This divergence is due to the maximum points for the specific rotations being reached at different temperatures for different wave-lengths. This ester thus shows very clearly that the points on the characteristic diagram cease to lie on straight lines when the maximum points are reached in the temperature-rotation curves; in fact, the diagram itself is only a temperature-rotation diagram for the ester, with the curvature of all the lines for different wave-lengths referred to a standard wave-length (λ 5461 Å.U.) which, by definition, is a straight line at 45°.

In the case of the *n*-butyl ester a similar result was obtained, but in all cases where the temperature-rotation curves did not approach maxima their characteristic diagrams were obtained, giving straight lines.

These investigations were carried out with a Schmidt and Hantsch polarimeter with a triple field, which was fitted with a direct vision spectroscope of the same make. The source of light consisted of an oxygen-coal gas flame, which impinged horizontally on a flat, vertical surface of thorium oxide, giving an intensely brilliant white light. The spectroscope was calibrated by means of Hartmann's dispersion formula (*Astrophys. J.*, 1898, **8**, 218), the error being less than 1 Å.U. Our calibration of the instrument agreed, within experimental error, with that given by Schmidt and Hantsch.

The errors in rotation measurements are greatest in the extreme red and violet ends of the spectrum, due to rapid falling off in luminosity of the field; the order of possible errors being 0.04° in the red part (λ 6708), 0.02° in the yellow (λ 5893), 0.04 — 0.05° in the blue (λ 4678), and 0.1° in the violet (λ 4359). The thermometers used were calibrated by reference to the University standards.

In all cases where rotation readings were taken of an ester exposed to a high temperature, the rotation value of the same specimen was determined at a low temperature and its rotation confirmed by means of the temperature-rotation curve. Also in the cases where maxima occurred in these curves, several unrecorded confirmatory sets of readings at temperatures in the neighbourhood of these maxima were taken.

EXPERIMENTAL.

Resolution of Lactic Acid.—The lactic acid used in these investigations was resolved by the fractional crystallisation of its morphine salt (Patterson, T., 1913, **103**, 2263) with the following slight modification.

Seventy-five c.c. of the syrupy acid (d 1.21) were boiled under reflux with 912 c.c. of water for 6—10 hours. To half of the solution, while still hot, 140 grams of morphine were added, the other half was neutralised with its equivalent of caustic soda (18.52 grams), and the solutions were mixed. On cooling and by evaporation, three crops of crystals of morphine *l*-lactate were obtained, which were crystallised twice from water. The salt was dissolved in warm water and ammonia added until all the alkaloid was precipitated. The morphine was filtered off and the solution of ammonium lactate was converted into its zinc salt.

Preliminary investigations showed that a salt of lactic acid was preferable to the free acid for esterification. The best results were obtained by the use of the zinc ammonium compound.

The solution of the ammonium salt was boiled with an excess of zinc oxide until the smell of ammonia was scarcely perceptible. The excess of zinc oxide was filtered off and on evaporation of the filtrate the zinc ammonium lactate crystallised out. This was

recrystallised from a small quantity of water and used in the preparation of the esters.

Rotation.—The zinc ammonium *l*-lactate gave $[\alpha]_D^{25}$ (in ammoniacal solution) $+10.09^\circ$ (concentration of the salt 3.47 grams in 50 c.c.). Patterson's value is $[\alpha]_D^{25} +10.09^\circ$ (concentration of the salt 4 grams in 50 c.c.).

Methyl l-Lactate.—To 25 grams of dry zinc ammonium *l*-lactate and 100 c.c. of dry methyl alcohol, 19.25 grams of concentrated sulphuric acid were slowly added. The mixture was heated on the water-bath for four hours, allowed to cool, the excess of sulphuric acid neutralised with finely powdered potassium carbonate, and the solution filtered from salts, which were extracted with dry ether. The solvents having been removed, the residue was distilled in a vacuum. After four fractionations, the ester had b. p. $32-33^\circ/8$ mm. (oil-bath temperature $70-75^\circ$). Yield 11 grams (55 per cent. of the theoretical).

There is much variation in the value of the optical rotation of the ester, as given by different workers.

	$[\alpha]_D^{25}$	t°	d_4^{25}	
Frankland	-15.00°	15°	1.1017	P., 1895, 11 , 54.
Walker	-11.10	13	1.100	T., 1895, 68 , 914.
Patterson	$+8.10$	16.7	1.0971	T., 1913, 103 , 2263.
	$+9.32$	56.0	1.0518	"
Present authors	$+8.15$	16.7	1.0970	"
	$+9.44$	56	1.0509	"

A peculiarity was noticed in the optical behaviour of one sample of the ester which had been kept for several days in a vacuum desiccator. The rotation of the ester ($[\alpha]_D^{25} +8.22^\circ$) increased in fifteen days to nearly twice this value ($[\alpha]_D^{25} +14.20^\circ$). This was possibly due to the formation of a lactide having a high rotation (Irving, T., 1899, **72**, 484).

Densities determined :

t°	10.7°	26.0°	52.4°	82.7°	119.0°
d_4^{25}	1.1037	1.0857	1.0556	1.0208	0.9782

The ester has complex rotatory dispersion.

λ (in Å.U.).	Temp.	d_4^{25}	Temp.	d_4^{25}	Temp.	d_4^{25}
	11.9°	1.1023.	16.5°	1.0970.	27.3°	1.0841.
α (1 dem.).	$[\alpha]_D^{25}$	α (1 dem.).	$[\alpha]_D^{25}$	α (1 dem.).	$[\alpha]_D^{25}$	α (1 dem.).
6708	$+6.82^\circ$	$+6.19^\circ$	$+6.97^\circ$	$+6.35^\circ$	$+7.16^\circ$	$+6.59^\circ$
6563	7.17	6.51	7.29	6.65	7.50	6.92
6438	7.51	6.82	7.61	6.94	7.81	7.21
6152	8.22	7.46	8.33	7.60	8.54	7.88
5893	8.82	8.01	8.92	8.14	9.21	8.50
5590	9.60	8.71	9.74	8.87	10.06	9.28
5324	10.36	9.40	10.52	9.59	10.83	9.99
5086	10.97	9.95	11.15	10.16	11.52	10.63
4861	11.49	10.43	11.71	10.67	12.10	11.16
4678	11.87	10.77	12.10	11.03	12.55	11.58
4455	12.30	11.16	12.56	11.45	13.12	12.10

	Temp. 56.5°.	$d_D^{56.5^\circ}$ 1.0509.	Temp. 84.9°.	$d_D^{84.9^\circ}$ 1.0184.	Temp. 115.3°.	$d_D^{115.3^\circ}$ 0.9826.
λ .	α (1 dem.).	$[\alpha]_D^{56.5^\circ}$.	α (1 dem.).	$[\alpha]_D^{84.9^\circ}$.	α (1 dem.).	$[\alpha]_D^{115.3^\circ}$.
6708	+7.51°	+7.15°	+7.90°	+7.76°	+8.08°	+8.23°
6563	7.90	7.51	8.28	8.13	8.53	8.69
6438	8.25	7.85	8.69	8.54	8.94	9.10
6152	9.06	8.63	9.55	9.37	9.89	10.07
5893	9.92	9.44	10.49	10.30	10.91	11.10
5590	10.82	10.29	11.54	11.33	12.10	12.31
5324	11.69	11.12	12.52	12.29	13.22	13.46
5086	12.51	11.90	13.47	13.23	14.27	14.52
4861	13.23	12.59	14.37	14.11	15.28	15.55
4678	13.85	13.18	15.10	14.83	16.13	16.41
4455	14.60	13.90	15.95	15.66	17.13	17.43

Ethyl 1-Lactate.—A mixture of 36 grams of dry zinc ammonium lactate, 195 c.c. of dry ethyl alcohol, and 27.8 grams of concentrated sulphuric acid was heated under reflux for four hours and treated as described for the methyl ester. Four fractional vacuum distillations yielded a product, b. p. 53°/15 mm. (oil-bath temperature 90—95°). Yield 13 grams (72 per cent. of the theoretical).

The data available for this ester are as follows:

		t° .	$[\alpha]_D^{t^\circ}$.	$d_D^{t^\circ}$.
Purdie and Williamson (T., 1899, 69, 827)	Ag salt	14°	-13.46	1.0415
Walker (T., 1895, 67, 919)	Acid and alcohol	14	-10.33	1.0423
Klimenko (<i>J. Russ. Chem. Soc.</i> , 1880, 12, 30)	Ag salt	19	-14.52	1.030
Purdie and Irvine (T., 1899, 72, 484)			-14.90	-
Frankland and Henderson (P., 1895, 11, 54)		20	-8.25	1.0925
Present authors		15	-17.90	1.044
		18.9	-11.26	1.0345

The ester prepared by the silver salt method gives high rotations due to the formation of an ether.

Densities determined:

t°	7.15°	20.4	40	77.2	119.6
$d_4^{t^\circ}$	1.0471	1.0324	1.0163	0.9688	0.9198

The ester exhibits complex rotatory dispersion.

	Temp. 8.5°.	$d_D^{8.5^\circ}$ 1.0461.	Temp. 18.9°.	$d_D^{18.9^\circ}$ 1.0346.	Temp. 53°.	$d_D^{53^\circ}$ 0.9953.
λ .	α (1 dem.).	$[\alpha]_D^{8.5^\circ}$.	α (1 dem.).	$[\alpha]_D^{18.9^\circ}$.	α (1 dem.).	$[\alpha]_D^{53^\circ}$.
6708	-8.83°	-8.44°	-9.06°	-8.75°	-9.61°	-9.66°
6563	9.22	8.81	9.50	9.18	10.03	10.08
6438	9.62	9.20	9.90	9.57	10.41	10.46
6152	10.50	10.04	10.77	10.41	11.40	11.46
5893	11.38	10.88	11.65	11.27	12.32	12.38
5590	12.52	11.97	12.81	12.39	13.63	13.69
5324	13.52	12.92	13.87	13.41	14.82	14.89
5086	14.52	13.88	14.94	14.44	15.99	16.05
4861	15.44	14.76	15.92	15.38	17.14	17.22
4678	16.33	15.61	16.88	16.32	18.25	18.34
4455	17.42	16.65	18.03	17.43	19.55	19.64
4359	17.95	17.16	18.57	17.95	20.11	20.20

λ .	Temp. 84°.	d_4^{25} 0.9607.	Temp. 113.7°.	$d_4^{113.7}$ 0.9261.
	α (1 dem.).	$[\alpha]_D^{25}$.	α (1 dem.).	$[\alpha]_D^{113.7}$.
6708	+9.94°	+10.35°	+10.06°	+10.86°
6563	10.34	10.76	10.45	11.31
6438	10.74	11.18	10.84	11.71
6152	11.74	12.22	11.94	12.89
5893	12.75	13.27	13.02	14.06
5590	14.06	14.63	14.37	15.52
5324	15.34	15.96	15.60	16.85
5086	16.59	17.27	16.89	18.23
4861	17.79	18.52	18.09	19.53
4678	18.91	19.68	19.21	20.74
4455	20.27	21.09	20.56	22.20
4359	20.90	21.75	21.17	22.86

n-Propyl *l*-Lactate.—This ester was prepared from 41 grams of dry zinc ammonium *l*-lactate, 40 grams of *n*-propyl alcohol, and 28.5 grams of concentrated sulphuric acid in a yield of 23 grams (52 per cent. of the theoretical). The ester was distilled four times in a vacuum, and then had b. p. 70–71°/16 mm. (oil-bath temperature 100°).

Comparative table of data for the ester.

B. p.	Wassmer and Guye. 60–61°/10–11 mm.	Present authors. 70–71°/16 mm.
d_4^{17}	0.994	1.0655
d_4^{25}	0.957	0.9660
n_D^{17}	~ 5.08° (in $\frac{1}{2}$ -dem. tube)	~ 6.60°
$[\alpha]_D^{17}$	~ 10.23°	~ 13.13°
$[\alpha]_D^{17}$	~ 13.50°	~ 17.37°

Densities determined :

t°	2.2°	17.0°	49.76°	87.99°	122.1°
d_4°	1.0203	1.0055	0.9717	0.9316	0.8965

The ester exhibits complex rotatory dispersion.

λ .	Temp. 3.5°.	$d_4^{3.5}$ 1.0191.	Temp. 27.9°.	$d_4^{27.9}$ 0.9940.	Temp. 68°.	d_4^{68} 0.9523.
	α (1 dem.).	$[\alpha]_D^{3.5}$.	α (1 dem.).	$[\alpha]_D^{27.9}$.	α (1 dem.).	$[\alpha]_D^{68}$.
6708	+10.16°	+10.97°	+10.27°	+10.33°	+10.34°	+10.86°
6563	10.58	10.38	10.69	10.75	10.80	11.34
6438	11.08	10.87	11.18	11.25	11.23	11.79
6152	12.06	11.83	12.19	12.26	12.26	12.87
5893	13.14	12.89	13.27	13.36	13.36	14.03
5590	14.44	14.17	14.60	14.69	14.74	15.48
5461	15.11	14.83	15.26	15.35	15.47	16.24
5324	15.97	15.67	16.06	16.16	16.32	17.14
5086	17.27	16.94	17.54	17.65	17.82	18.74
4861	18.65	18.31	18.94	19.05	19.37	20.34
4678	19.81	19.44	20.21	20.33	20.62	21.65
4455	21.28	20.88	21.71	21.84	22.15	23.26
4359	21.85	21.44	22.34	22.53	22.94	24.09

γ^*

λ .	Temp. 102.1°.	$d_D^{102.1^\circ}$ 0.9170.	Temp. 115.7°.	$d_D^{115.7^\circ}$ 0.9030.
α (1 dem.).	$[\alpha]_D^{102.1^\circ}$.	α (1 dem.).	$[\alpha]_D^{115.7^\circ}$.	
6708	+10.40°	+11.33°	+10.43°	+11.56°
6563	10.90	11.89	10.96	12.14
6438	11.26	12.28	11.34	12.56
6152	12.40	13.52	12.46	13.80
5893	13.42	14.63	13.48	14.93
5590	14.90	16.25	14.94	16.54
5461	15.63	17.05	15.73	17.42
5324	16.47	17.96	16.55	18.33
5086	18.13	19.77	18.18	20.13
4861	19.67	21.45	19.78	21.91
4678	20.97	22.82	21.13	23.40
4455	22.49	24.53	22.63	25.05
4359	23.32	25.43	23.48	26.00

n-Butyl *l*-Lactate.—To 32.5 grams of dry zinc ammonium *l*-lactate, mixed with 100 grams of *n*-butyl alcohol (b. p. 118°/747 mm.), 14 c.c. of concentrated sulphuric acid were slowly added, the mixture being then heated on a water-bath for five hours and subsequently treated as in the cases of the esters previously described. After four vacuum fractionations, the ester was obtained, b. p. 77°/10 mm. (oil-bath temperature 110°). The ester is a highly refractive, sweet-smelling, colourless liquid. Yield 12 grams (40 per cent. of the theoretical). Wassmer and Guye (*loc. cit.*) give the following data for this ester: B. p. 70–73°/10–11 mm.; $[\alpha]_D^{17.0^\circ} + 11.7^\circ$; $d_4^{16.5^\circ}$ 0.9850 (the rotation given includes a correction of +1.26° for partial inactivity of the materials used in the formation of the ester).

Our values are: $[\alpha]_D^{17.0^\circ} + 14.7^\circ$; $d_4^{17.0^\circ}$ 0.9856.

Densities determined:

t°	8.4°	27.6°	54.8°	80.0°	100.3°	136.8°
d_4°	0.9937	0.9744	0.9475	0.9227	0.9020	0.8651

The ester is complex in rotatory dispersion, and maxima occur in the temperature-rotation curves.

λ .	Temp. 10.4°.	$d_D^{10.4^\circ}$ 0.9919.	Temp. 27.3°.	$d_D^{27.3^\circ}$ 0.9748.	Temp. 57.8°.	$d_D^{57.8^\circ}$ 0.9446.
α (1 dem.).	$[\alpha]_D^{10.4^\circ}$.	α (1 dem.).	$[\alpha]_D^{27.3^\circ}$.	α (1 dem.).	$[\alpha]_D^{57.8^\circ}$.	
6708	10.14°	+10.22°	10.29°	+10.56°	10.41°	+11.02°
6563	10.60	10.69	10.72	11.10	10.85	11.48
6438	11.01	11.12	11.16	11.45	11.31	11.98
6152	12.05	12.18	12.21	12.53	12.41	13.14
5893	13.04	13.18	13.28	13.63	13.50	14.30
5590	14.42	14.54	14.66	15.03	14.92	15.80
5324	15.77	15.88	16.06	16.47	16.45	17.41
5086	17.18	17.28	17.45	17.90	17.87	18.92
4861	18.54	18.70	18.88	19.37	19.38	20.52
4678	19.72	19.87	20.09	20.61	20.73	21.90
4455	21.17	21.34	21.62	22.17	22.36	23.67
4359	21.80	21.98	22.20	22.78	22.95	24.30

λ .	Temp.	$d_4^{20.3^\circ}$	Temp.	$d_4^{20.5^\circ}$	Temp.	$d_4^{20.1^\circ}$
	91.3°.	0.9110.	104.5°.	0.8977.	126.1°.	0.8758.
	α (1 dem.).	$[\alpha]_D^{20.3^\circ}$.	α (1 dem.).	$[\alpha]_D^{20.5^\circ}$.	α (1 dem.).	$[\alpha]_D^{20.1^\circ}$.
6708	+10.47°	+11.48°	+10.37°	+11.55°	+10.06°	+11.49°
6563	10.94	12.01	10.84	12.08	10.57	12.07
6438	11.43	12.55	11.32	12.61	11.04	12.60
6152	12.54	13.77	12.46	13.88	12.18	13.91
5893	13.71	15.05	13.55	15.10	13.21	15.09
5590	15.15	16.62	15.06	16.77	14.68	16.77
5324	16.63	18.26	16.59	18.48	16.20	18.50
5086	18.09	19.86	18.05	20.10	17.71	20.20
4861	19.72	21.65	19.65	21.90	19.22	21.95
4678	21.11	23.17	21.06	23.46	20.68	23.61
4455	23.00	25.25	23.02	25.59	22.50	25.70
4359	23.72	26.04	23.74	26.45	23.32	26.63

n-Amyl *l*-Lactate.—This was prepared from 22 grams of dry zinc ammonium *l*-lactate, 48 grams of *n*-amyl alcohol (b. p. 137.1°/750 mm.), and 10.8 c.c. of concentrated sulphuric acid as in the case of the *n*-butyl ester. After four vacuum distillations, the product had b. p. 87.6–87.9°/8–9 mm. Yield of crude ester 16 grams (50 per cent. of the theoretical).

No comparative data are available for this ester. The rotation after the fourth (and also after a fifth) distillation was $\alpha_D^{20} + 12.27^\circ$. A specimen of the ester from the third distillation gave a higher rotation, $\alpha_D^{20} + 13.78^\circ$.

Readings were taken at 32° and 69.7°, but at higher temperatures the rotation had decreased to $\alpha_D^{70} + 9.00^\circ$. The ester which had been exposed to high temperature was redistilled and its rotation rose to the value obtained after the third fractionation, $\alpha_D^{20} + 13.75^\circ$. Subsequent vacuum distillations failed to reduce this high value, and a fresh quantity of the ester was prepared.

The extraordinary behaviour of this ester is probably due to the comparative ease with which it forms a lactide, having possibly a higher rotation than the ester itself, similar to the case of the methyl ester. According to the theory that an open-chain carbon compound has a helical structure, it would seem that this ester might be analogous in behaviour to the first member of the series. It is difficult to make accurate observations at high temperatures, and the readings were taken rapidly when the ester was in a pure state, for the substance causing the increase in rotatory power, once formed, is difficult to eliminate by distillation.

In a second preparation, the following quantities were used: 22 grams of dry zinc ammonium *l*-lactate, 15.4 grams of concentrated sulphuric acid, 35 grams of pure *n*-amyl alcohol. In this case, a much better yield was obtained (22 grams, 70 per cent. of the theoretical). After four vacuum distillations, the pure ester was obtained having b. p. 109.5–110.5°/21.5 mm. (oil-bath temperature

130°). This sample had identical rotation with that obtained from the fourth vacuum distillation in the previous preparation. Accordingly, sets of readings were taken at 13.9°, 94.7°, and 127°. After the ester had cooled from the last two temperatures, its rotation was observed in order to detect internal change or racemisation. Although in each case the ester was tinged slightly yellow, the rotation on cooling lay on the temperature-rotation curve, thus showing that no changes had taken place.

Densities determined :

t°	13.3°	21.2°	56.8°	78°	117.5°	139.5°
d_4^t	0.9717	0.9638	0.9297	0.9090	0.8711	0.8500

The ester shows complex rotatory dispersion.

λ .	Temp. 13.9°.		Temp. 32°.		Temp. 69.8°.	
	α (1 dem.).	$[\alpha]_D^{13.9}$.	α (1 dem.).	$[\alpha]_D^{32}$.	α (1 dem.).	$[\alpha]_D^{69.8}$.
6708	-9.25°	-9.53°	+9.29°	+9.75°	+9.57°	+10.44°
6563	9.71	10.00	9.78	10.29	9.98	10.89
6438	10.11	10.41	10.16	10.66	10.44	11.39
6152	11.11	11.43	11.20	11.63	11.41	12.45
5893	12.12	12.49	12.15	12.74	12.35	13.47
5590	13.35	13.74	13.41	14.08	13.70	14.94
5324	14.69	15.13	14.75	15.47	15.18	16.56
5086	16.01	16.59	16.14	16.92	16.48	17.98
4861	17.29	17.80	17.42	18.28	17.80	19.42
4678	18.38	18.95	18.57	19.47	19.09	20.82
4455	19.82	20.41	20.10	21.09	20.62	22.49
4359	20.43	21.04	20.72	21.70	21.30	23.23

λ .	Temp. 94.7°.		Temp. 127°.	
	α (1 dem.).	$[\alpha]_D^{94.7}$.	α (1 dem.).	$[\alpha]_D^{127}$.
6708	+9.63°	+10.78°	+9.57°	+11.10°
6563	10.05	11.25	9.95	11.54
6438	10.48	11.73	10.41	12.08
6152	11.43	12.79	11.41	13.24
5893	12.37	13.85	12.29	14.26
5590	13.76	15.41	13.74	15.94
5324	15.23	17.05	15.15	17.56
5086	16.54	18.52	16.44	19.07
4861	17.84	19.97	17.70	20.53
4678	19.14	21.43	19.11	22.17
4455	20.85	23.34	20.73	24.04
4359	21.52	24.09	21.43	24.86

n-Hexyl *l*-Lactate.—*n*-Hexyl alcohol was prepared from *n*-butyl alcohol by a method given in a private communication from Dr. Pickard, which is a modification of one given in the University of Illinois Bulletin, XVIII, Oct., 1920, No. 6 (Adams, Kamni, and Marvel). Eighteen grams of hexyl alcohol (b. p. 156–157°/745 mm.), 21 grams of dry zinc ammonium *l*-lactate, and 14.7 grams of concentrated sulphuric acid were heated together on a water-bath for five hours. Instead of first neutralising the reaction mixture

by simple addition of powdered potassium carbonate, the volume was made up to 400 c.c. with dry ether in order to increase the rate of filtration and also to precipitate the potassium hexyl sulphate formed on addition of potassium carbonate. The solution was neutralised, filtered, and the ether distilled off. The ester was distilled in a vacuum four times and then boiled at 107–108°/16 mm. (oil-bath temperature 145°). Yield 13.5 grams (44 per cent. of the theoretical).

No comparative data are available for this ester.

It had $[\alpha]_D^{20} + 12.21^\circ$, $[M]_D^{20} + 21.25^\circ$, and d_4^{20} 0.9520.

Densities determined :

t°	2.0°	16.6°	44.8°	81.5°	119.2°
d_4°	0.9682	0.9553	0.9298	0.8969	0.8630

The ester exhibits complex rotatory dispersion.

λ .	Temp. 6°.	d_4^{20} 0.9647.	α (1 dem.).	$d_4^{21.7}$ 0.9504.	Temp. 62.9°.	$d_4^{22.7}$ 0.9138.
6708	+ 9.10°	+ 9.50°	+ 9.28°	+ 9.76°	+ 9.63°	+ 10.54°
6563	9.36	9.70	9.62	10.12	10.07	11.02
6438	9.66	10.01	9.92	10.44	10.39	11.37
6152	10.50	10.88	10.70	11.26	11.24	12.30
5893	11.38	11.80	11.64	12.25	12.27	13.43
5590	12.60	13.06	12.90	13.58	13.64	14.93
5461	13.16	13.64	13.48	14.18	14.19	15.53
5324	13.76	14.26	14.20	14.94	14.98	16.39
5086	15.00	15.55	15.37	16.17	16.29	17.83
4861	16.23	16.82	16.69	17.56	17.73	18.96
4678	17.23	17.86	17.77	18.70	18.88	20.66
4455	18.77	19.46	19.21	20.21	20.35	22.27
4359	19.33	20.04	19.85	20.89	21.04	23.05

λ .	Temp. 83.3°.	$d_4^{23.3}$ 0.8952.	α (1 dem.).	Temp. 107.6°.	$d_4^{25.6}$ 0.8733.
6708	+ 9.78°	+ 10.93°	+ 9.94°	+ 11.38°	
6563	10.20	11.40	10.36	11.86	
6438	10.54	11.77	10.72	12.28	
6152	11.50	12.85	11.70	13.40	
5893	12.50	13.96	12.72	14.57	
5590	13.86	15.48	14.10	16.15	
5461	14.46	16.15	14.72	16.86	
5324	15.27	17.06	15.53	17.78	
5086	16.65	18.60	16.97	19.43	
4861	18.15	20.28	18.51	21.20	
4678	19.31	21.57	19.71	22.57	
4455	20.81	23.25	21.23	24.25	
4359	21.51	24.03	21.95	25.13	

n-Heptyl L-Lactate.—A mixture of 24 grams of dry zinc ammonium lactate, 40 grams of *n*-heptyl alcohol (b. p. 175.5°), and 17 grams of concentrated sulphuric acid was heated on the water-bath for six hours. The mixture was subsequently treated as in the case of hexyl lactate. After four vacuum fractionations, a product was obtained

having b. p. $117^{\circ}/10$ mm. (oil-bath temperature 150°). Yield 71 per cent. of the theoretical.

Rotation of the ester (unaltered by a further vacuum distillation) $[\alpha]_D^{20} + 11.35^{\circ}$.

Wassmer and Guye give $[\alpha]_D^{20} - 12.24^{\circ}$ (heptyl *d*-lactate).

A second preparation of the ester gave a rotation identical with the first, although the time of contact with the sulphuric acid was only three instead of six hours.

Densities determined:

t°	9.6°	34°	61.5°	90.8°	112.4°	139.7°
d_4^t	0.9521	0.9301	0.9054	0.8790	0.8596	0.8350

The ester exhibits complex rotatory dispersion.

λ .	Temp. 10.3° .	$d_4^{10.3^{\circ}}$ 0.9516.	$[\alpha]_D^{10.3^{\circ}}$.	Temp. 33° .	$d_4^{33^{\circ}}$ 0.9310.	$[\alpha]_D^{33^{\circ}}$.	Temp. 71.7° .	$d_4^{71.7^{\circ}}$ 0.8961.	$[\alpha]_D^{71.7^{\circ}}$.
	α (1 dem.).			α (1 dem.).			α (1 dem.).		
6708	$+8.08^{\circ}$		$+8.49^{\circ}$	$+8.20^{\circ}$		$+8.81^{\circ}$	$+8.31^{\circ}$		$+9.27^{\circ}$
6563	8.46		8.89	8.58		9.22	8.71		9.72
6438	8.84		9.29	8.97		9.64	9.09		10.15
6152	9.73		10.22	9.86		10.59	9.98		11.14
5893	10.63		11.17	10.76		11.55	10.90		12.16
5590	11.81		12.41	11.97		12.86	12.12		13.53
5324	12.97		13.63	13.13		14.10	13.32		14.87
5086	14.14		14.86	14.38		15.45	14.58		16.28
4861	15.30		16.08	15.55		16.70	15.78		17.61
4678	16.35		17.18	16.64		17.87	16.90		18.87
4455	17.62		18.51	17.96		19.30	18.31		20.44
4359	18.19		19.11	18.58		19.95	18.95		21.14

λ .	Temp. 99.7° .	$d_4^{99.7^{\circ}}$ 0.8709.	$[\alpha]_D^{99.7^{\circ}}$.	Temp. 128.9° .	$d_4^{128.9^{\circ}}$ 0.8446.	$[\alpha]_D^{128.9^{\circ}}$.
	α (1 dem.).			α (1 dem.).		
6708	-8.23°		-9.45°	-8.05°		-9.53°
6563	8.62		9.00	8.43		9.98
6438	9.01		10.35	8.83		10.46
6152	9.92		11.40	9.75		11.54
5893	10.81		12.42	10.65		12.61
5590	12.06		13.85	11.88		14.07
5324	13.26		15.23	13.05		15.45
5086	14.52		16.67	14.31		16.94
4861	15.73		18.06	15.49		18.34
4678	16.86		19.36	16.58		19.63
4455	18.25		20.96	17.98		21.29
4359	18.92		21.73	18.62		22.05

Readings of rotations were taken at 153.7° , but on cooling to a lower temperature the decrease of rotation indicated racemisation or decomposition.

n-Octyl *l*-Lactate.—This ester was prepared similarly to hexyl lactate, from *n*-octyl alcohol (b. p. $195.5^{\circ}/760$ mm.). Yield 16 grams (50 per cent. of the theoretical) from 24 grams of dry zinc ammonium *l*-lactate. After four vacuum distillations, the ester had b. p. $137^{\circ}/11$ mm. (oil-bath temperature 160 – 170°) and

$[\alpha]_D^{25} + 9.31^\circ$. Wassmer and Guye give b. p. 126—128°/11 mm. and $[\alpha]_D^{25} + 12.08^\circ$ (by calculation).

Densities determined :

d_4^{25}	13.7°	58.3°	89.3°	111°	134.3°
d_4^{25}	0.9356	0.8973	0.8713	0.8523	0.8321

The ester exhibits complex rotatory dispersion, and maxima occur in the temperature-rotation curves.

λ.	Temp. 17.6°.		Temp. 34.4°.		Temp. 65°.	
	α (1 dem.).	$[\alpha]_D^{17.6}$.	α (1 dem.).	$[\alpha]_D^{34.4}$.	α (1 dem.).	$[\alpha]_D^{65}$.
6708	+6.75°	+7.24°	+6.80°	+7.41°	+6.88°	+7.71°
6563	7.00	7.51	7.06	7.69	7.15	8.02
6438	7.23	7.74	7.30	7.96	7.41	8.31
6152	7.96	8.54	8.01	8.73	8.13	9.12
5893	8.69	9.32	8.75	9.53	8.92	10.00
5590	9.62	10.32	9.70	10.56	9.89	11.18
5324	10.52	11.30	10.64	11.60	10.85	12.16
5086	11.43	12.25	11.57	12.60	11.81	13.24
4861	12.48	13.38	12.66	13.79	12.99	14.56
4678	13.43	14.41	13.64	14.85	14.04	15.69
4455	14.54	15.60	14.85	16.17	15.37	17.22
4359	15.08	16.17	15.46	16.84	15.96	17.90

λ.	Temp. 103.5°.		Temp. 134.1°.	
	α (1 dem.).	$[\alpha]_D^{103.5}$.	α (1 dem.).	$[\alpha]_D^{134.1}$.
6708	+6.71°	+7.81°	+6.43°	+7.73°
6563	6.99	8.15	6.75	8.11
6438	7.29	8.50	7.05	8.47
6152	8.01	9.33	7.81	9.38
5893	8.83	10.28	8.65	10.39
5590	9.80	11.41	9.66	11.60
5324	10.78	12.54	10.68	12.83
5086	11.76	13.69	11.63	13.98
4861	12.90	15.02	12.77	15.33
4678	14.04	16.33	13.96	16.75
4455	15.51	18.07	15.51	18.63
4359	16.11	18.77	16.16	19.40

Readings were taken at 158°, but on checking the rotation of the ester at a lower temperature, decomposition was indicated.

n-Nonyl *l*-Lactate.—The *n*-nonyl alcohol used was prepared from *n*-octyl alcohol (see under *n*-hexyl lactate). Fifteen grams of nonyl alcohol (b. p. 107—108°/15 mm.), 12.6 grams of dry zinc ammonium *l*-lactate, and 8.8 grams of concentrated sulphuric acid were heated together on a water-bath for five hours. The subsequent treatment was as described under hexyl lactate. Yield 11 grams (50 per cent. of the theoretical). The ester, fractionated four times in a vacuum, had b. p. 153—154°/20 mm. (oil-bath temperature 180°), $[\alpha]_D^{25} + 9.19^\circ$, $[M]_D^{25} + 19.85^\circ$, and d_4^{25} 0.9191.

No comparative data are available for this ester.

Densities determined :

616 ROTATORY DISPERSION OF THE ESTERS OF LACTIC ACID. PART I.

t°	4-6°	18-57°	45-6°	83-2°	130-5°
d_4^{25}	0-9320	0-9201	0-8977	0-8661	0-8265

The ester exhibits complex rotatory dispersion.

λ .	Temp. 4-8°.	$d_4^{48^{\circ}}$ 0-9319.	Temp. 23-4°.	$d_4^{25^{\circ}}$ 0-9161.	Temp. 74-5°.	$d_4^{74^{\circ}}$ 0-8734.
λ .	α (1 dm.).	$[\alpha]_D^{18^{\circ}}$.	α (1 dm.).	$[\alpha]_D^{25^{\circ}}$.	α (1 dm.).	$[\alpha]_D^{74^{\circ}}$.
6708	+6-63°	+7-12°	+6-75°	+7-37°	+6-89°	+7-89°
6563	6-87	7-37	7-02	7-66	7-18	8-22
6438	7-06	7-58	7-24	7-90	7-42	8-50
6152	7-68	8-24	7-88	8-60	8-14	9-32
5893	8-30	8-91	8-52	9-30	8-84	10-12
5590	9-20	9-87	9-46	10-34	9-86	11-29
5461	9-64	10-34	9-94	10-85	10-39	11-90
5324	10-24	10-99	10-54	11-51	11-00	12-59
5086	11-12	11-93	11-46	12-51	11-99	13-73
4861	12-10	12-99	12-46	13-66	13-10	15-00
4678	12-94	13-89	13-28	14-50	14-00	16-03
4455	13-88	14-90	14-34	15-65	15-08	17-27
4359	14-32	15-37	14-80	16-16	15-63	17-90

λ .	Temp. 100-5°.	$d_4^{100^{\circ}}$ 0-8516.	Temp. 128°.	$d_4^{128^{\circ}}$ 0-8286.
λ .	α (1 dm.).	$[\alpha]_D^{100^{\circ}}$.	α (1 dm.).	$[\alpha]_D^{128^{\circ}}$.
6708	+6-99°	+8-21°	+7-07°	+8-53°
6563	7-30	8-57	7-40	8-93
6438	7-56	8-88	7-67	9-26
6152	8-26	9-48	8-29	10-00
5893	9-00	10-57	9-20	11-10
5590	10-10	11-86	10-30	12-43
5461	10-60	12-45	10-77	13-00
5324	11-20	13-15	11-41	13-77
5086	12-20	14-33	12-34	14-89
4861	13-32	15-64	13-52	16-32
4678	14-24	16-72	14-49	17-49
4455	15-41	18-09	15-71	18-96
4359	16-01	18-80	16-33	19-71

Summary.

(i) In the homogeneous condition, the active *n*-alkyl lactates, from the methyl to the nonyl member, exhibit complex rotatory dispersion of a normal and similar type.

(ii) The molecular rotations of the series give a smooth curve, reaching a maximum at the hexyl ester (or the heptyl ester at lower temperatures). The maximum at the hexyl ester and the abnormal value for the amyl ester may be explained by assuming the helical structure of the carbon chain.

(iii) With two exceptions, the rotatory power of the esters increases with temperature. The temperature effect in all cases is slight. *n*-Butyl and *n*-octyl lactates show maxima in the temperature-rotation curves.

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[Received, January 15th, 1923.]

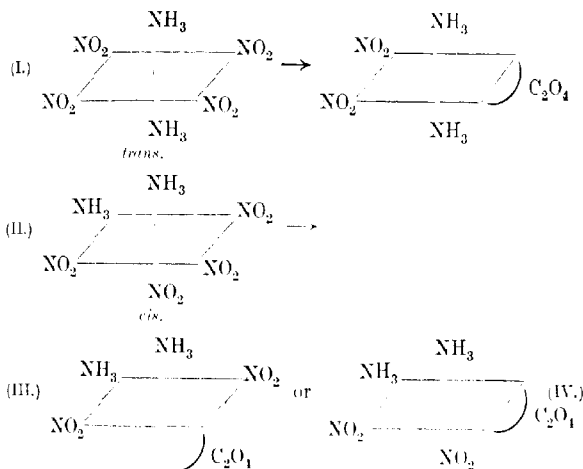
LXXII.—*Inorganic Complex Salts. Part II. Erdmann's Salt and its Derivatives.*

By WILLIAM THOMAS.

WERNER's classic researches on the inorganic complex salts have enabled us to give definite configurations to most of the isomerides occurring in this group of compounds. A definite configuration, however, has not been given to Erdmann's salt, ammonium tetranitrodiamminecobaltate, one of the first known complex salts of cobalt (*J. pr. Chem.*, 1866, **97**, 385). It appeared of interest to ascertain which of the formulæ (I and II) should be assigned to this compound.

It is evident that replacement of nitro-groups in the *trans*-diammine compound would not yield an asymmetric molecule, but replacement of one or more nitro-groups of the *cis*-diammine complex might result in a molecule resolvable into optical antipodes.

It was found that oxalic acid acts on the compound, two nitro-groups being replaced by one oxalato-group. The possible modes of replacement are best seen from the following figures.



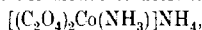
The product from the *trans*-diammine complex is thus ammonium oxalato-*cis*-dinitro-*trans*-diamminecobaltate, in which a plane of symmetry passes through the acid groups.

In the case of the *cis*-diammine structure two products are possible, ammonium oxalato-*trans*-dinitro-*cis*-diamminecobaltate

(III) and ammonium oxalato-*cis*-dinitro-*cis*-diamminecobaltiate (IV). In the sequel these will be referred to as the *trans-cis*- and the *cis-cis*-complexes, respectively. Of these, the *cis-cis*-complex alone is asymmetric and therefore should be resolvable.

The product of the action of oxalic acid on Erdmann's salt was converted into the barium salt, which was separated by fractional crystallisation into isomerides belonging to the rhombohedral and monoclinic systems, respectively, the former being the more soluble and present in larger quantity (4 : 1). Attempts to resolve these by means of alkaloid sulphates were successful in the case of the rhombohedral crystalline compound only, indicating that it is the *cis-cis*-complex (IV). The non-resolvable compound (monoclinic) must therefore be the *trans-cis*-complex (III). The corresponding malonato-derivative was also prepared, but could not be resolved.

Attempts to prepare the dioxalato-derivative,



and the dimalonato-derivative were unsuccessful.

Jaeger and his collaborators examined the crystals of the optically active antipodes of a large number of complex salts of the type MeX_3 (*Rec. trav. chim.*, 1919, **38**, 171), in which the groups round the central atom are identical. These complex salts in aqueous solution have enormous rotatory power, but the tendency to develop hemihedral forms is very feeble. Whereas enantiomorphism of molecular configuration is the one and only condition for development of optical activity, Jaeger suggested that chemical contrast of the groups round the central metallic atom would possibly favour the formation of hemihedral crystals of the antipodes. The foregoing asymmetric derivative of Erdmann's salt contains different groups round the central atom, but optically active crystals have not been obtained, racemisation taking place during crystallisation.

EXPERIMENTAL.

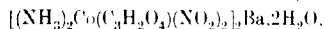
Erdmann's salt, prepared by Jørgensen's method (*Z. anorg. Chem.*, 1898, **17**, 476), was purified by repeated recrystallisation and converted into ammonium oxalato-dinitrodiamminecobaltiate by the action of a concentrated solution of oxalic acid (Jørgensen, *ibid.*, 1896, **11**, 440), subsequent deposition of small, rhombohedral and of monoclinic crystals indicating the formation of two products. The ammonium salt having been converted into the barium salt by means of a saturated solution of barium chloride (1 equiv.), the isomerides were separated by fractional crystallisation, the one yielding the rhombohedral crystals being by far the less soluble (Found : for the rhombohedral crystals, Co = 15.94;

Ba = 18.54; H_2O = 7.30. $[(NH_3)_2Co(C_2O_4)(NO_2)_2]_2Ba \cdot 3H_2O$ requires Co = 16.01; Ba = 18.49; H_2O = 7.33 per cent. Found: for the monoclinic crystals, Co = 16.45; Ba = 19.18; H_2O = 5.25. $[(NH_3)_2Co(C_2O_4)(NO_2)_2]_2Ba \cdot 2H_2O$ requires Co = 16.39; Ba = 19.10; H_2O = 5.00 per cent.).

Barium was weighed as sulphate. To estimate the cobalt, the complex salt was destroyed by heating it with sodium hydroxide, and the cobalt, thereby precipitated as the hydroxide, was dissolved in sulphuric acid and reprecipitated from the neutral solution as ammonium cobalt phosphate, which was ignited to the pyrophosphate, $Co_2P_4O_7$. The water of crystallisation was estimated by keeping the finely divided crystals at 95° until there was no further loss of weight.

Resolution of the Complex Salt.—Equivalent quantities of the barium salt and an alkaloid sulphate were mixed in solution and the filtrate subjected to fractional crystallisation. Brucine and cinchonine were unsuitable for the purpose, hydrolysis taking place and the free base being precipitated. With strychnine, however, two fractions containing *strychnine l-oxalato-cis-dinitro-cis-diammine-cobaltate* were obtained; subsequent fractions contained the free alkaloid. When *d*-phenylethylamine was employed as the active base, the first fraction contained the *d*-complex salt. These active salts were converted by aqueous potassium iodide into the active potassium salts, which had $[\alpha]_D : 1.54^\circ$, whence $[M]_D 481.5^\circ$ (Found: Co = 17.75; H_2O = 5.55. $[(NH_3)_2Co(C_2O_4)(NO_2)_2]K \cdot H_2O$ requires Co = 17.87; H_2O = 5.45 per cent.).

Barium Malonatodinitro-cis-diamminecobaltate.



was prepared by mixing saturated solutions of equivalent quantities of oxalic acid and Erdmann's salt, adding barium chloride solution, and allowing the very soluble barium salt to separate (the ammonium salt is even more soluble). Two derivatives are again possible as in the case of the oxalato-derivative, but no separation could be effected (Found: Co = 15.66; Ba = 18.34; H_2O = 4.86. $[(NH_3)_2Co(C_3H_2O_4)(NO_2)_2]_2Ba \cdot 2H_2O$ requires Co = 15.78; Ba = 18.38; H_2O = 4.82 per cent.).

Crystals of these complex compounds were examined by Miss I. E. Knaggs (T., 1922, **121**, 2069).

NOTE.—Since the completion of the above work, Riesenfeld and Clement have published a paper (Z. anorg. Chem., 1922, **124**, 1) in which they conclude that Erdmann's salt is the *trans*-diammine compound, because they did not succeed in resolving its derivatives.

LXXIII.—*The Preparation of Xylose from Maize Cobs.*

By ARTHUR ROBERT LING and DINSHAW RATTONJI NANJI.

THE preparation of xylose from maize cobs has in recent years been exhaustively studied by Hudson and Hardinge (*J. Amer. Chem. Soc.*, 1918, **40**, 1601), La Forge and Hudson (*J. Ind. Eng. Chem.*, 1918, **10**, 925), and Monroe (*J. Amer. Chem. Soc.*, 1919, **41**, 1002). Recently, while engaged on some problems in connexion with the fermentation of sugars with different micro-organisms, we found it necessary to prepare xylose in considerable quantity. Hudson and Hardinge's method (*loc. cit.*) was at first employed, but after having repeatedly worked with several kilograms of the cobs following exactly the instructions given by these authors, we found their method required some modification.

The broken cobs (1 kilo.) are soaked in 2 per cent. ammonia solution, sufficient to cover them, and kept over-night. The cobs are then washed free of ammonia with hot tap-water and boiled under reflux with 8 litres of 7 per cent. sulphuric acid for exactly two hours. The main portion of the liquor is decanted from the cobs, without filtering, into a 12-litre earthenware jar, and the remainder of the extract is recovered by pressing the residue in a hand-press. The total extract, while still hot, is neutralised with the requisite quantity of precipitated chalk. The neutralisation takes place readily and does not require more than thirty minutes.

Judging from our experience, we do not recommend the alternative procedure of Hudson and Hardinge to neutralise with lime. Whilst there is no special purpose served by using lime, it has the distinct disadvantage of causing the decomposition of some of the dissolved sugar. The use of barium carbonate recommended by Monroe is not economical when xylose is to be prepared in quantity.

The precipitate of calcium sulphate is filtered through a Buchner funnel and the precipitate well washed with boiling water. The cold straw-coloured liquor after neutralisation is treated with 20 c.c. of 10 per cent. neutral lead acetate solution for every litre of the liquor. The lead precipitate is filtered off and the lead removed with hydrogen sulphide. The filtrate from the lead sulphide, which is pale yellow, is boiled with norit (20 grams) and filtered when all the hydrogen sulphide has been expelled. The filtrate at this stage is practically colourless, and is ready for the final concentration.

When this lead treatment is omitted, the neutral liquor possesses a strong tendency to froth when evaporation under reduced pressure is attempted, so much so as to render the concentration process

very difficult. The liquor obtained as above, however, after the lead treatment does not behave in this way, and the subsequent concentration under reduced pressure is carried out without any difficulty. This tendency to froth is due to the presence of a substance of the saponin class which the lead treatment removes from solution.

The colourless filtrate obtained above is then concentrated under reduced pressure to a thin syrup and treated with three times its volume of 95 per cent. alcohol. The precipitated calcium sulphate is filtered off and the alcoholic solution is then once again concentrated under reduced pressure to a viscous syrup. The pale yellow syrup thus obtained is ready for the crystallisation of xylose, for which either alcohol or glacial acetic acid may be employed. To crystallise from alcohol, the viscous syrup is dissolved in twice its volume of 95 per cent. alcohol, when the xylose crystallises out in a few hours. When glacial acetic acid is employed, the syrup is treated with half its volume of glacial acetic acid, and the crystallisation of xylose takes place immediately. It may, however, be remarked here that the syrup obtained under the above conditions is not free from glucose and therefore the use of alcohol is to be preferred to that of acetic acid when xylose is to be prepared in a state of purity. The crystals of xylose obtained above are collected on a Buchner funnel, washed with 95 per cent. alcohol and then with absolute alcohol, and dried in a desiccator. The yield of xylose obtained having the correct specific rotatory power and melting point was uniformly 10—12 per cent. of the cobs used.

We desire to express our thanks to Mr. W. S. Shaw for his assistance in carrying out this work.

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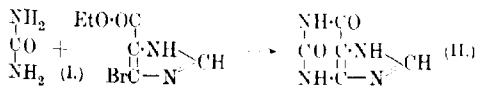
UNIVERSITY OF BIRMINGHAM.

[Received, January 31st, 1923.]

LXXIV.—*Bromination of Glyoxaline-4-carboxyanilide.*

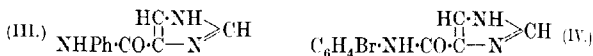
By HAROLD KING and WILLIAM OWEN MURCH.

THE primary object of this investigation was the preparation of 4-bromoglyoxaline-5-carboxylic acid with the view of synthesising xanthine (II), by condensation of the ester (I) with carbamide.

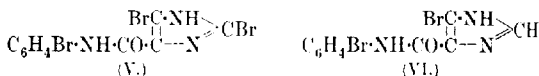


Hitherto syntheses of purine derivatives have only been effected *via* the pyrimidine ring, although the complementary process, starting with the glyoxaline ring, has frequently been suggested (Windaus and Knoop, *Beit. Physiol. Path.*, 1905, **6**, 392; Johnson, *J. Amer. Chem. Soc.*, 1914, **36**, 338; Winterstein and Trier, "Die Alkaloide," p. 315; Hopkins, T., 1916, **109**, 629; Fargher and Pyman, T., 1919, **115**, 217). Whilst the primary object has been attained, the small yields have hitherto precluded systematic attempts to condense the ester with carbamide.

The method of preparation adopted was the bromination of glyoxaline-4-carboxyanilide (III), which can be obtained in quantity by Fargher and Pyman's process (*loc. cit.*), using two molecular proportions of bromine in glacial acetic acid solution. The main products are *glyoxaline-4-carboxy-p-bromoanilide* (IV) and *2:5-dibromoglyoxaline-4-carboxy-p-bromoanilide* (V), of which about

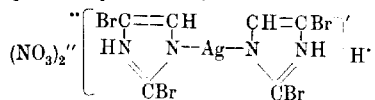


equal weights are obtained. The remaining products of the reaction are *5-bromoglyoxaline-4-carboxy-p-bromoanilide* (VI), which is obtained in smaller yield, accompanied by a *substance*, melting at 247°, containing 50.8 per cent. of bromine, a value somewhat less than that required for an equimolecular mixture of di- and tri-bromoglyoxalinecarboxyanilides. This substance was only isolated pure in small quantity, and no means has been found of preparing the dibromoanilide perfectly free from it.



The constitution of these bromo-derivatives follows from an examination of their products of hydrolysis. Glyoxaline-4-carboxy-*p*-bromoanilide (IV), on hydrolysis by boiling with concentrated hydrochloric acid, gives *p*-bromoaniline and glyoxaline-4-carboxylic acid. 2:5-Dibromoglyoxaline-4-carboxy-*p*-bromoanilide (V), on hydrolysis under pressure with hydrobromic acid, gives *p*-bromoaniline, 2:4-dibromoglyoxaline, and 2-bromoglyoxaline, the proportions of the latter two depending on the conditions employed. The 2:4-dibromoglyoxaline obtained agrees with that prepared by Balaban and Pyman by decarboxylation of 2:5-dibromoglyoxaline-4-carboxylic acid (T., 1922, **121**, 957). It gives a very sparingly soluble additive compound with silver nitrate in acid solution, the composition agreeing with $2\text{C}_3\text{H}_2\text{N}_2\text{Br}_2 \cdot \text{AgNO}_3 \cdot \text{HNO}_3$. The constitution of this interesting product may be represented on the

basis of Werner's view of the constitution of complex salts, by analogy with ammonium salts $\left[\begin{smallmatrix} \text{H} & \text{H} \\ & \text{N} \\ \text{H} & \text{H} \end{smallmatrix} \right] \text{Cl}'$ and with the compound $[\text{AgI}]\text{H}'$, if it be assumed that the silver atom is substituted for the imino-hydrogen of one of the glyoxaline nuclei as in the silver salts of glyoxalines formed in ammoniacal solution. The additive compound may, therefore, be written :



the silver atom holding the nuclei together by co-valence whilst the H' and $(\text{NO}_3)_2''$ are held by electrovalence. 2:5-Dichloroglyoxaline appears to form a similar compound, and Wallach and Böhringer (*Annalen*, 1877, **184**, 50) have described an additive product of silver nitrate and methylehloroglyoxaline nitrate, but the other mono- and tri-bromoglyoxalines examined by us failed to give insoluble silver compounds in acid solution. The formation of such sparingly soluble silver compounds in acid solution is unusual, but xanthine and theobromine both give precipitates, containing silver nitrate, in nitric acid solution. We have not had in hand 4:5-dihalogenated glyoxalines for comparison with their isomerides in this respect.

2-Bromoglyoxaline has not previously been described. It melts at 207° and its constitution follows because it is not identical with 4-bromoglyoxaline, prepared by Balaban and Pyman. It is characterised by its sparingly soluble *picrate* and its *nitrate*. This disposes of the last of the possible C-substituted bromoglyoxalines.

When 2:5-dibromoglyoxaline-4-carboxy-*p*-bromoanilide is hydrolysed under pressure with concentrated hydrochloric acid, the main product is 2:5-dichloroglyoxaline, the two bromine atoms having been replaced by chlorine.

5-Bromoglyoxaline-4-carboxy-*p*-bromoanilide (VI), on hydrolysis with hydrobromic acid, gives 4-bromoglyoxaline-5-carboxylic acid, the primary object of this investigation, and 4-bromoglyoxaline, the proportions depending on the conditions employed. 4-Bromoglyoxaline proved to be identical with the product isolated by Balaban and Pyman (*loc. cit.*) by reduction of 4:5-dibromoglyoxaline.

EXPERIMENTAL.

Bromination of Glyoxaline-4-carboxyanilide. Isolation of Mono-, Di-, and Tri-bromoglyoxaline-4-carboxyanilides.—To glyoxaline-

4-carboxyanilide (93.5 grams), dissolved in glacial acetic acid (500 c.c.), a solution of bromine (55 c.c.; 2 mols.) in glacial acetic acid (200 c.c.) was added slowly during half an hour, the temperature being kept below 20°. The crystalline solid, A, which separated on keeping over-night was collected and extracted twice on the boiling water-bath, each time with 2 litres of water. The aqueous filtrate, on cooling, deposited 12 grams of a mixture of mono- and di-bromoglyoxaline-4-carboxyanilides, and the filtrate from these, on making alkaline, gave almost pure monobromoglyoxaline-4-carboxyanilide (54.0 grams). The remainder of A was extracted four times with 2 litres of 3 per cent. hydrochloric acid. On cooling, 16.5 grams of crude dibromoglyoxaline-4-carboxyanilide separated, the filtrate depositing a negligible quantity of material on neutralisation. The insoluble solid A (56 grams) now consisted of slightly impure tribromoglyoxaline-4-carboxyanilide.

Glyoxaline-4-carboxy-p-bromoanilide crystallises from four times its weight of boiling glacial acetic acid in colourless needles containing two molecules of acetic acid, which are lost at 100° (Found: loss = 32.2. $C_{10}H_8ON_3Br \cdot 2C_2H_4O_2$ requires loss = 30.2 per cent.). It is very sparingly soluble in boiling water and separates on cooling in glistening leaflets, m. p. 273–274° (Found: Br = 30.1. $C_{10}H_8ON_3Br$ requires Br = 30.0 per cent.). It is sparingly soluble in the other usual organic solvents, and insoluble in sodium hydroxide solution, and it gives crystalline salts with acids.

Hydrolysis of Glyoxaline-4-carboxy-p-bromoanilide.—The anilide was hydrolysed by boiling with concentrated hydrochloric acid for seven hours. The solution was evaporated to dryness under reduced pressure, made alkaline with ammonia, and the *p*-bromoaniline extracted with ether. The extract was acetylated and gave, on crystallisation from alcohol, *p*-bromoacetanilide, melting at 166–167° (Found: Br = 36.9. Calc., Br = 37.3 per cent.). The ammoniacal liquor was concentrated to a small bulk and made faintly acid to Congo-paper. Glyoxaline-4-carboxylic acid separates on keeping. It was identified by comparison of its melting point and crystalline form with those of an authentic specimen.

2 : 5-Dibromoglyoxaline-4-carboxy-p-bromoanilide crystallises from twelve and a half times its weight of boiling glacial acetic acid in plates. It occasionally crystallises from the same solvent in fine needles with one molecule of acetic acid (Found: loss at 100° = 12.3. $C_{10}H_8ON_3Br_2 \cdot C_2H_4O_2$ requires loss = 12.4 per cent. Found: on plate form, Br = 56.4. $C_{10}H_8ON_3Br_2$ requires Br = 56.6 per cent.). In ethyl or methyl alcohol and in ethyl acetate it is sparingly soluble, but it dissolves readily in hot acetone; in chloroform, benzene, or xylene it is practically insoluble. It is

untouched by cold aqueous acids. With 2*N*-sodium hydroxide it forms a crystalline sodium salt, soluble on dilution, but precipitated only by prolonged passage of carbon dioxide. It is readily soluble on warming in *N*/2-sodium carbonate solution and gives no coloration with Pauly's reagent. It melts at 257—258° with decomposition.

Hydrolysis of 2 : 5-Dibromoglyoxaline-4-carboxy-p-bromoanilide with Hydrochloric Acid. Isolation of 2 : 5-Dichloroglyoxaline.—Ten grams of the tribromoanilide were hydrolysed in sealed tubes with 50 c.c. of 32 per cent. hydrochloric acid at 150° for three hours. The solution was evaporated to dryness, the residue dissolved in a small volume of water, made alkaline with sodium carbonate, and extracted six times with ether. The ethereal extract (6.6 grams) was steam-distilled, *p*-bromoaniline passing over in the distillate. On acetylation, it gave 4.6 grams of *p*-bromoacetanilide, which, on recrystallisation from spirit, melted at 166—167° (Found : Br = 37.0 per cent.). The ethereal extract of the substance non-volatile in steam amounted to 2.23 grams. On recrystallisation from benzene or, better, from water, it melted at 184—185° and had all the qualitative reactions of a dihalogenated glyoxaline. Analysis showed, however, that it consisted of about 95 per cent. of dichloroglyoxaline and 5 per cent. of dibromoglyoxaline [Found : N = 19.9, 19.7; AgCl ÷ AgBr = 203.7, 202.7, 203.8. $C_3H_2N_3Cl_2$ (95 per cent.) + $C_3H_2N_3Br_2$ (5 per cent.) requires N = 20.3; AgCl ÷ AgBr = 203.4 per cent.]. The possibility is not excluded that some of the bromo-constituent may be present as a mixed chlorobromoglyoxaline. It was not found possible to isolate a purer dichloroglyoxaline owing to the formation of mixed crystals.

2 : 5-Dichloroglyoxaline, as obtained above, dissolves to the extent of 3 per cent. in boiling water and crystallises in prismatic needles. It is very soluble in ethyl acetate, but very sparingly so in chloroform or benzene. It is soluble in ether and can be extracted from aqueous solutions by this solvent. It is soluble in hydrochloric acid (more concentrated than 3*N*) and is precipitated on dilution. It is slowly soluble in dilute sodium carbonate solution, readily soluble in dilute sodium hydroxide, and is precipitated by excess of carbon dioxide. In nitric acid solution, it forms a sparingly soluble additive product with silver nitrate (see corresponding dibromoglyoxaline).

Hydrolysis of 2 : 5-Dibromoglyoxaline-4-carboxy-p-bromoanilide with Hydrobromic Acid. Isolation of Mono- and Di-bromoglyoxalines.—The products obtained depend on the strength of hydrobromic acid used. Two grams of tribromoanilide, heated in a sealed tube for three hours with 10 c.c. of 24 per cent. hydrobromic acid, gave 0.4

gram of unchanged solid, and on removal of excess of hydrobromic acid and dilution with water, 0.25 gram of 2 : 5-dibromoglyoxaline. On recrystallisation from water, the latter melted at 197–198° (Found : Br = 70.6. Calc., Br = 70.7 per cent.). The qualitative reactions are in agreement with those described for this substance by Balaban and Pyman.

Ten grams of the tribromoanilide were hydrolysed in sealed tubes, 4 grams with 24 per cent., and 6 grams with 30 per cent., hydrobromic acid at 150° for three hours. After removal of 1.5 grams of unchanged material, the solutions were evaporated to dryness under reduced pressure and the residue, on dilution with 10 c.c. of water, gave 0.4 gram of 2 : 5-dibromoglyoxaline. The filtrate was made neutral to Congo-paper by addition of sodium hydrogen carbonate and extracted with ether, which removed some *p*-bromoaniline, tar, and dibromoglyoxaline. The aqueous liquor was then made alkaline and extracted with ether, and the ethereal residue extracted with cold chloroform. The solid left undissolved (1.05 grams) was monobromoglyoxaline.

2-Bromoglyoxaline crystallises from water in long, prismatic needles, m. p. 207°. It is readily soluble in dilute hydrochloric acid and in dilute sodium hydroxide. From the latter it is precipitated by carbon dioxide (Found : Br = 54.2; N = 18.9. $C_3H_3N_2Br$ requires Br = 54.4; N = 19.1 per cent.). With Pauly's reagent, it gives a deep orange colour.

The *picrate* crystallises from water, in which it is sparingly soluble, in very long, glistening, yellow needles, m. p. about 232° with decomposition (Found : Br = 21.3. $C_3H_3N_2Br \cdot C_6H_3O_7N_3$ requires Br = 21.2 per cent.).

The *nitrate* crystallises from water in stout needles and decomposes violently at 137° (Found : Br = 37.9. $C_3H_3N_2Br \cdot HNO_3$ requires Br = 38.1 per cent.).

The *silver nitrate additive compound of 2 : 5-dibromoglyoxaline nitrate* was obtained by dissolving 0.2 gram of dibromoglyoxaline in 3 c.c. of 3*N*-nitric acid and adding 5.5 c.c. of *N*/10-silver nitrate. The additive product separated immediately in fine needles, the yield being 0.3 gram (Found : Br = 15.7. $2C_3H_3N_2Br_2 \cdot AgNO_3 \cdot HNO_3$ requires Br = 15.8 per cent.).

5-Bromoglyoxaline-4-carboxy-p-bromoanilide.—This substance is readily and quantitatively separated from any accompanying glyoxaline-4-carboxy-*p*-bromoanilide by extraction with very dilute hydrochloric acid, in which the monobromo-derivative is alone soluble. It can also be practically quantitatively separated from 2 : 5-dibromoglyoxaline-4-carboxy-*p*-bromoanilide by extraction with hot 3 per cent. hydrochloric acid, in which the tribromoanilide is

insoluble. The yield of material free from mono- and tri-bromoglyoxalinecarboxyanilides is about 22 grams.

5-Bromoglyoxaline-4-carboxy-p-bromoanilide crystallises from glacial acetic acid in fine, soft, white, silky needles, m. p. 245–246°. It is soluble in about six parts of boiling acetic acid (Found: Br = 47.1, 47.1, 47.1. $C_{10}H_7ON_3Br_3$ requires Br = 46.3 per cent.). In spite of numerous attempts by various methods, a product with a lower bromine value was never obtained. On keeping, the glacial acetic acid mother-liquors deposit small, hard, clear tablets of a substance containing a higher percentage of bromine and melting with effervescence at 247° (Found: Br = 50.9 per cent.). The reactions of this substance and of dibromoglyoxalinecarboxyanilide are almost identical. After repeated crystallisation from glacial acetic acid, dibromoglyoxalinecarboxyanilide retains a small percentage of this substance, as is shown by the analyses. A mixture of the two melted at 235°. Both form crystalline sodium salts on treatment with 2*N*-sodium hydroxide solution and are dissolved on dilution; both are reprecipitated in needles on passing carbon dioxide through the solutions. This substance of unknown constitution is, however, very sparingly soluble in boiling glacial acetic acid when obtained pure. It has not been isolated in sufficient quantity for complete analysis. It is also formed when pure glyoxaline-4-carboxy-*p*-bromoanilide is brominated (Found: Br = 50.7 per cent.).

Hydrolysis of 5-Bromoglyoxaline-4-carboxy-p-bromoanilide with Hydrobromic Acid.—The products depend on the strength of acid used.

With 24 per cent. Hydrobromic Acid.—Two grams of the dibromoglyoxalinecarboxyanilide were heated in a sealed tube with 10 c.c. of hydrobromic acid (24 per cent.) for three hours at 150°. The solution was evaporated to dryness under reduced pressure, the residue dissolved in water, and sodium hydrogen carbonate added until the solution was faintly acid to Congo-paper. The crystalline bromoglyoxalinecarboxylic acid which separated was washed with ether to remove adhering *p*-bromoaniline and then weighed 0.6 gram. The filtrate was thoroughly extracted with ether, and, on removal of the latter, crude *p*-bromoaniline was left (0.63 gram). On dissolving in a little chloroform, 0.05 gram of bromo-acid was deposited. The aqueous filtrate was then made alkaline with sodium carbonate and extracted with ether, which on evaporation left a further quantity of *p*-bromoaniline. The two fractions of *p*-bromoaniline were combined and when acetylated weighed 1.0 gram. On recrystallisation, *p*-bromoacetanilide was obtained, melting at 167–168° (Found: Br = 37.2 per cent.).

With 30 per cent. Hydrobromic Acid.—When 2 grams of the anilide were hydrolysed as above with 30 per cent. hydrobromic acid, 4-bromoglyoxaline was isolated. The acid liquor was evaporated to dryness under reduced pressure and the residue made alkaline with sodium hydrogen carbonate and extracted with ether. The ethereal extract (1.35 grams) was distilled in steam, *p*-bromoaniline passing over. The non-volatile portion was treated with charcoal and on concentration gave 0.2 gram of 4-bromoglyoxaline, melting at 132–133°. A portion was converted into picrate, which crystallised in leaflets melting at 164–165° (Found: Br = 21.1. Calc., Br = 21.2 per cent.). The properties of the 4-bromoglyoxaline, its nitrate, and its picrate agreed with those described by Balaban and Pyman.

The original alkaline aqueous liquor was concentrated to a small volume under diminished pressure, and on making faintly acid to Congo-paper, 5-bromoglyoxaline-4-carboxylic acid separated to the extent of 0.7 gram.

5-Bromoglyoxaline-4-carboxylic acid is soluble in 50 parts of boiling water and crystallises in clusters of leaflets, m. p. 265° with effervescence. It is soluble in dilute hydrochloric or sulphuric acid and is precipitated by concentrated hydrochloric acid as the hydrochloride in small compact rosettes. With 3*N*-nitric acid, it forms a sparingly soluble *nitrate*, soluble on dilution. It is soluble in sodium hydrogen carbonate and forms a sparingly soluble salt with 2*N*-ammonia. The ammoniacal solution gives a silver salt on addition of silver nitrate. The acid couples with Pauly's reagent, giving a deep orange colour, but not so red as that given by glyoxaline-4-carboxylic acid (Found: Br = 41.9; N = 14.8. $C_6H_3O_2N_2Br$ requires Br = 41.8; N = 14.7 per cent.).

The *ethyl ester* was prepared substantially as described by Pyman (T., 1916, 109, 200) for ethyl glyoxaline-5-carboxylate. It separates as a crystalline powder on adding saturated potassium carbonate solution to an aqueous solution of the hydrochloride. It is most conveniently recrystallised from toluene and separates in thin, glistening plates melting at 170–171°. It is readily soluble in acetone, alcohol, ethyl acetate, or benzene, but almost insoluble in low- or high-boiling petroleum (Found: N = 13.0. $C_6H_7O_2N_2Br$ requires N = 12.8 per cent.).

The original acetic acid mother-liquors of the bromination of glyoxalinecarboxyanilide were concentrated to small bulk and poured into water. After making alkaline, the total solid weighed 16 grams. This was put through the same process of fractionation as the main batch of material, namely, extraction with 250 c.c. of 3 per cent. hydrochloric acid on the boiling water-bath. The insoluble

material was highly coloured and could only be partly resolved into its constituents. Tribromoglyoxalinecarboxyanilide was, however, isolated. The acid-soluble extract gave 6.3 grams of almost pure monobromoglyoxalinecarboxyanilide.

Bromination of Glyoxaline-4-carboxy-p-bromoanilide.—When pure glyoxaline-4-carboxy-p-bromoanilide was treated in glacial acetic acid solution with bromine (1 mol.) and the products were worked up as in the case of the bromination previously described, the same products were isolated, the 5-bromoglyoxaline-4-carboxy-p-bromoanilide being again obtained mixed with the substance melting at 247° and containing 50.7 per cent. of bromine.

Bromination of 5-Bromoglyoxaline-4-carboxy-p-bromoanilide.—One gram of the dibromoanilide ($\text{Br} = 47.1$ per cent.) was brominated in glacial acetic acid solution (1 mol. Br). After standing for twenty-four hours in the dark, the acetic acid was removed by distillation under reduced pressure and the residue dissolved in dilute sodium hydroxide solution. On passing carbon dioxide for a short time, a voluminous precipitate was obtained, from which, on extraction with hot 3 per cent. hydrochloric acid, the substance, melting at 247° and containing 50.8 per cent. of bromine was removed. The residue which was left on crystallisation from glacial acetic acid separated in warts melting above 280° . The main product of the bromination was isolated from the alkaline liquors by prolonged passage of carbon dioxide and was identified as 2:5-dibromoglyoxaline-4-carboxy-p-bromoanilide.

One of the authors desires to thank Professor F. L. Pyman, F.R.S., for frequent opportunity of discussing the chemistry of the glyoxalines and for his acquiescence in the publication of these results.

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[Received, February 15th, 1923.]

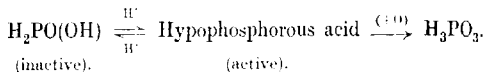
LXXV.—*Studies in Hypophosphorous Acid. Part V.* *Its Reaction with Silver Nitrate.*

By ALEC DUNCAN MITCHELL.

SEVERAL reactions have now been studied (Mitchell, T., 1920, **117**, 1322; 1921, **119**, 1266; 1922, **121**, 1624) in which hypophosphorous acid effects reduction of inorganic substances, and certain regularities have been noted in the rate of reduction. This rate is

independent of the concentration of these substances (provided they are not too dilute) and is the same in each case for similar concentrations of hypophosphorous acid *molecules* and hydrogen-ions, the latter acting catalytically. The inference is drawn that some rearrangement of the hypophosphorous acid molecule is a necessary antecedent to reaction, and that the more active form thus produced exists, to a very small extent, in equilibrium with the molecules, the equilibrium being continuously displaced in favour of the more active form as it is utilised in the course of the reaction. It must be emphasised that the velocity coefficient obtained throughout these experiments is based on the assumption of an equilibrium and is that of the direct change: it fails to represent the course of the reaction in dilute solutions unless it is considered in conjunction with a reverse change. Similarly, it was shown that the catalytic effect of the hydrogen-ion can be expressed mathematically only if it is assumed to accelerate the reverse change also.

The general scheme of the reactions may therefore be represented as



There is a certain amount of indirect evidence that the active form is $\text{HP}(\text{OH})_2$ as opposed to the well-established constitution $\text{H}_2\text{PO}(\text{OH})$ for the ordinary (inactive) form. It was pointed out previously (T., 1922, 121, 1624) that the oxy-acids of phosphorus and their esters show a pronounced tendency to favour the quinquevalent condition, and a tervalent condition, such as that suggested for the active form, would be associated with greater activity. This view is further supported by the fact that the compounds of the type $\text{R}_2\text{PO}(\text{OH})$ do not exhibit reducing powers with, for instance, silver nitrate, whereas those of the type $\text{RHPO}(\text{OH})$ do so (R being an organic radicle). Such reducing capacity is sometimes ascribed to the presence of a hydrogen atom attached directly to the phosphorus atom, but this cannot be the primary cause, since hypophosphorous acid (as such) has no reducing power, at any rate in a large number of cases, in spite of the fact that it possesses two such hydrogen atoms. It appears to be far more probable that the more immediate cause is that the hydrogen atom is capable of migrating in such a way as to form a tervalent compound.

Some organic derivatives of hypophosphorous acid are being studied in the hope that their behaviour will give more definite evidence on this point. In the meantime, it is justifiable to assume that the active form of the acid is isomeric with the inactive form,

and one has thus the essential features of tautomerism according to the accepted definition as "reversible isomeric change," the hydrogen-ion functioning as a true catalyst in that it does not affect the equilibrium, but only the rate at which it is attained.

It is believed that this is the first instance in which tautomerism of an inorganic compound has been put on a quantitative basis, although the possibility of it is suggested in the case of several inorganic acids by analogy with their alkyl derivatives, for example, the symmetrical and unsymmetrical esters of sulphurous and phosphorous acids, and the nitro-paraffins and alkyl nitrites derived from nitrous acid. In the case of sulphurous acid, the possibility has recently been shown to be a probability by Morgan and Smith (T., 1922, 121, 1956) from a consideration of the co-ordination number of the salicylatotetramminocobaltic complex in its bisulphite, and by Bennett (T., 1922, 121, 1795) in view of the fact that sulphurous acid, at the moment of its liberation from its salts, is capable of an auto-reduction which it does not otherwise exhibit. Undoubtedly, the rate of interconversion of the tautomeric forms of these compounds is usually far too rapid to be demonstrated except by methods such as that employed by Usherwood (T., 1922, 121, 1604), who, from measurements of the ratio of the specific heats of hydrocyanic acid at various temperatures, deduced that they are affected by a heat-change which is ascribed to a shift in the equilibrium between the two forms.

It seemed of interest to submit the reactions of hypophosphorous acid to a further examination in order to ascertain, if possible, the precise nature of its tautomeric form. It was hoped that such evidence might be obtained from a kinetic study of the reactions when they were due only to the active form and were so slow as not to be affected by the preliminary change. In the three cases cited, this was done with very dilute solutions of iodine, mercuric chloride, and cupric chloride, respectively, and in several other cases now being studied the required conditions are fulfilled by relatively stronger solutions. The reaction with silver nitrate does not lend itself to this purpose except when this reagent is so dilute—certainly weaker than $N/100$ —as to be unsuitable for rapid and accurate analysis, but the results are now communicated because they give strong confirmation of the uniformity of the tautomeric change by their close agreement with the results obtained in the cases previously published.

The rapidity of the reaction between the active form and the silver-ion renders the reverse effect of the equilibrium negligible, and therefore one has to consider only the direct tautomeric change of the molecules. This is represented by the equation $ds/dt =$

$kl_t(1 - \alpha_t)h_t$, where s is the amount of phosphorous acid produced in time t , h_t is the concentration of hydrogen-ions at that time, and l_t is similarly that of unchanged hypophosphorous acid, of which α_t is the degree of ionisation. If h and l represent the corresponding quantities initially, then $l_t = l - s$, and $h_t = h + ms$, since h is nearly (but not quite) a linear function of s ; $(1 - \alpha_t)$ is not a simple function of s , but is regarded as constant for the purpose of integration, and allowance is subsequently made; with these approximations, one has

$$(h + ml)(1 - \alpha_R)kt = 2.3 (\log l/(l - s) + \log(h + ms)/h).$$

In employing this equation for any particular time, one uses that value of α which obtains half-way through the period, α_H , and the value of m which represents the change of h with s for that period.

The values of k thus obtained give a mean of 130×10^{-5} , which agrees with those found for the three other reductions studied, 128×10^{-5} , 134×10^{-5} , and 111×10^{-5} , although in all cases the values decrease slightly for lower concentrations of hypophosphorous acid. This is believed to be due to the uncertain effect on its ionisation of substances which do not contain a common ion, and for which no correction has been applied.

EXPERIMENTAL.

The stoichiometric equation for the oxidation of hypophosphorous acid to phosphorous acid is $2\text{AgNO}_3 + \text{H}_3\text{PO}_2 + \text{H}_2\text{O} = 2\text{Ag} + 2\text{HNO}_3 + \text{H}_3\text{PO}_3$, but, in the case of silver nitrate, one cannot, as in some cases, neglect the further stage of the reaction, so that one has also $4\text{AgNO}_3 + \text{H}_3\text{PO}_2 + 2\text{H}_2\text{O} = 4\text{Ag} + 4\text{HNO}_3 + \text{H}_3\text{PO}_4$, and the necessary correction is applied as follows. Nitric and hypophosphorous acids are monobasic when titrated with either methyl-orange or phenolphthalein as indicator, whereas phosphorous and phosphoric acids are monobasic with the former indicator and dibasic with the latter. If, therefore, l represents the initial number of hypophosphorous acid molecules, and s_1 and s_2 the number oxidised to phosphorous and phosphoric acids, respectively, at any definite time, one has a methyl-orange titre of $(l - s_1 - s_2) + (2s_1 + 4s_2) + (s_1 + s_2) = l + 2s_1 + 4s_2$, and a phenolphthalein titre of $(l - s_1 - s_2) + (2s_1 + 4s_2) + (2s_1 + 2s_2) = l + 3s_1 + 5s_2$, the titres being bracketed to show those due to (1) hypophosphorous acid, (2) nitric acid, and (3) total phosphorous and phosphoric acids. The difference between the two titres gives $(s_1 + s_2) = s$, and hence $(l - s)$, and the increase in the methyl-orange titre over that at zero-time gives $2s_1 + 4s_2$, corresponding to the amount of nitric acid produced.

The correction thus introduced caused a reduction in the value of s amounting usually to not more than 6 per cent., but made the method rather more sensitive to experimental error than in the case of mercuric chloride, where the results were based on the total increase in titre.

The calculation of results follows the same lines as in previous communications. The effect of the silver nitrate on the ionisation of the nitric acid produced (and, therefore, indirectly on that of the hypophosphorous acid) was allowed for in the same way as in the case of copper chloride, the ionisation data of silver nitrate and nitric acid being assumed to be the same as those of sodium chloride and hydrochloric acid, respectively, since the data for these are known very accurately (Bray and Hunt, *J. Amer. Chem. Soc.*, 1911, **33**, 781) and any small differences would not appreciably affect the slight corrections in the hydrogen-ion concentration necessitated by the presence of the silver nitrate. Allowance is made throughout for the presence of about 5 per cent. of phosphorous acid initially present in the hypophosphorous acid.

Test experiments showed that, under the conditions of experiment, (1) nitric and hypophosphorous acids had no appreciable mutual action, and (2) the nitric acid did not redissolve the precipitated silver within the time of an experiment unless it became stronger than $N/5$.

Other experimental details were very similar to those used when investigating the reaction with iodine, the temperature being 25° as before. The method of analysis usually adopted was to allow a definite volume of the reaction mixture to flow into 50 c.c. of water containing excess of sodium chloride, and then to titrate with sodium hydroxide (free from carbonate), using first methyl-orange and then phenolphthalein as indicators. The precipitated silver was carried down by the silver chloride and did not prevent the obtaining of sharp end-points. Another method, adopted with the weakest silver solutions (in which the oxidation of phosphorous acid would be negligible), was to add the desired volume of reaction mixture to a slight excess of $N/50$ -ammonium thiocyanate solution, filter and wash the precipitate, and back-titrate the excess of thiocyanate with $N/50$ -silver nitrate solution: hypophosphorous acid was found not to affect the accuracy of this method in blank experiments.

The detail for calculation of experiment IV is shown in the following table. The values of s and the concentration of the nitric acid are obtained as outlined above, and the degrees of ionisation are found by graphic methods as explained in the iodine experiments; H' represents the concentration of hydrogen-ions

derived from the nitric acid, α the degree of ionisation of the hypophosphorous acid, H_p the hydrogen-ions to which it gives rise, and the other quantities shown are obtained as described when the integration was discussed. All concentrations are in gram-molecules per 200 litres, as before, in order to avoid small decimals,

t .	s .	$l-s$.	HNO_3 .	H' .	α .	H_p .	h .	$1-\alpha_H$.	m .	$k \times 10^3$.
0	—	11.08	—	—	0.645	7.42	7.42	—	—	—
20	0.77	10.31	1.58	1.47	0.616	7.09	8.56	0.370	1.480	124
40	1.67	9.41	3.62	3.34	0.587	6.76	10.10	0.384	1.605	122
60	2.68	8.40	5.83	5.38	0.558	6.42	11.80	0.399	1.635	121
80	3.90	7.18	8.38	7.73	0.527	6.06	13.79	0.413	1.632	125
100	5.16	5.92	11.02	10.18	0.500	5.75	15.93	0.428	1.650	126
120	6.20	4.88	13.67	12.51	0.478	5.50	18.01	0.442	1.706	122
140	7.37	3.71	15.92	14.70	0.459	5.28	19.98	0.458	1.703	124
160	8.16	2.92	17.33	16.00	0.450	5.18	21.18	0.473	1.688	120
										Mean 123

$AgNO_3 = 19.80$. When $s = 0$, $\alpha_{AgNO_3} = 0.842$, $\alpha_{HNO_3} = 0.923$,
 $s = 4$, 0.840 , 0.923 ,
 $s = 8$, 0.837 , 0.922 .

The amount of nitric acid formed after a further period of twelve hours corresponded to 19.82, thus, by its agreement with the initial amount of silver nitrate, 19.80, showing that the analytical method agrees with the stoicheiometric equation.

The following table summarises the other experiments, values at zero-time being shown:

Expt.	$AgNO_3$.	l .	α .	H_p and h .	$k \times 10^3$.
1	19.6	21.90	0.544	12.35	136
2	4.9	21.84	0.545	12.15	138
3	39.2	21.90	0.544	12.35	137
4	19.8	11.08	0.645	7.42	123
6	49.0	21.90	0.544	12.35	134
7	196.0	21.90	0.544	12.35	134
8	9.9	10.77	0.650	7.20	118
9	37.1	10.77	0.650	7.20	114
10	48.8	26.54	0.520	14.21	143
					Mean 130

Experiment 2 was carried out by the second analytical method and showed no falling off in the value of k until the concentration of silver nitrate became less than 2.0 ($= N/100$). Experiment 5 was an attempt, by the same method, to follow the reaction beyond this, but it appeared to be complete in eight minutes and the accuracy of the analytical results did not warrant any deductions therefrom.

Summary.

(1) Hypophosphorous acid reduces silver nitrate at the same rate as, *ceteris paribus*, it reduces iodine, mercuric chloride, or cupric chloride.

(2) This rate is independent of the concentration of the substance

undergoing reduction, provided it exceeds a definite value, which is $N/50$ in the case of silver nitrate, and is ascribed to a change involving the formation of an active form of the acid.

(3) In view of the uniformity of these reductions and of the definite evidence that the above change is reversible, it is suggested that one has here the first substantiated case of tautomerism in an inorganic acid.

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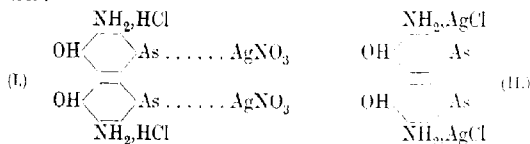
[Received, February 3rd, 1923.]

LXXVI.—*Silver Salvarsan.*

By WILLIAM HERBERT GRAY.

IN 1913, Ehrlich directed attention to the fact that salvarsan (diaminodihydroxyarsenobenzene dihydrochloride) had the remarkable property of forming stable complexes with salts of the heavy metals. In these, the ionic reactions of the metal had disappeared; for instance, they could be made alkaline, and thus suitable for intravenous injection, without losing their solubility. Sodium silver salvarsan (Brit. Pat. 1247/1914) has come into prominence for the treatment of the highly resistant late stages of syphilis, and therefore it is of great importance that the real nature of these products should be ascertained.

Two views have hitherto been advanced, (1) that silver salvarsan and sodium silver salvarsan* are co-ordination compounds, (2) that sodium silver salvarsan is a mixture containing colloidal silver. Ehrlich and Karrer (*Ber.*, 1915, 48, 1634) considered that salvarsan formed an additive compound (I) with two molecules of silver nitrate, in which the silver was attached by residual valency to the arsenic:



Karrer (*Ber.*, 1919, 52, 2321) still maintains this, and states that sodium silver salvarsan is formed simply by replacement of the phenolic hydrogen by sodium. Binz and his collaborators (*Arch.*

* For convenience, the author here uses the names "sodium silver salvarsan" and "silver salvarsan" to distinguish between the alkali and non-alkali reaction products of salvarsan and silver nitrate.

Inst. exper. Ther. Georg Speyer-Hause, 1919, 8, 25; *Ber.*, 1920, 53, [B], 416), on the contrary, considered that the silver was attached to nitrogen as in (II), but have recently suggested that there are two series of compounds, one in which silver is attached to nitrogen, the other in which it is attached to arsenic (*Ber.*, 1922, 55, [B], 3826). The possibility, on the other hand, that the dark coloured sodium silver salvarsan might contain colloidal silver was suggested by Kolle (*Deut. med. Woch.*, 1918, 1177) and investigated by Bauer (*Arb. Inst. exper. Ther. Georg Speyer-Hause*, 1919, 8, 45; *Ber.*, 1920, 53, [B], 416), who found that the solution passed unchanged through parchment paper and collodion membranes and concluded that colloidal silver was not present, and by Raiziss and Gavron (*J. Pharm. Exper. Ther.*, 1922, 20, 163), who obtained the contrary result, arsenic passing the parchment but no silver, and suggested that sodium silver salvarsan was a mixture of sodium salvarsan and colloidal silver.

The author has for some time been investigating the nature of silver salvarsan and sodium silver salvarsan, in solutions in methyl alcohol as used by Ehrlich and Karrer, and aqueous solutions as used by Binz.

In solutions in methyl alcohol, it was found that if an excess of ether were used for precipitation, as is customary in the salvarsan series, a solid could be obtained from the reaction mixture of diaminodihydroxyarsenobenzene hydrochloride and silver nitrate having the same silver-content as that of Ehrlich and Karrer, who did not state the amount of ether taken. If, however, the alcoholic solution were added to a comparatively small quantity of ether, a solid, soluble in water, was precipitated which contained arsenic, silver, and chlorine in the atomic ratios 2 : 7.1 : 6.4. This contains more silver and less arsenic than could correspond to a co-ordination compound: it therefore consists of colloidal silver chloride, reversibly soluble owing to the small amount of arsenic compound now precipitated with it, the chief constituent of which is probably the hitherto undescribed diaminodihydroxyarsenobenzene dimitate. This view receives support by the observation that in more concentrated methyl-alcoholic solutions, if the alcohol were dry, silver chloride was precipitated without the addition of ether. Under similar experimental conditions, solutions of sodium silver salvarsan in methyl alcohol yielded colloidal silver oxide, reversibly soluble in water.

In the case of aqueous solutions, emphasis has been laid by previous workers on the difficulty of investigating the interaction of salvarsan and silver nitrate owing to the similar solubility of all the substances concerned. Binz, Bauer, and Hallstein (*Arb.*

Inst. exper. Ther. Georg Speyer-Hause, 1919, **8**, 25) could not, for this reason, elucidate the nature of a solution containing two molecular proportions of silver nitrate. It is now found that all the silver is removed from aqueous solutions of both silver salvarsan and sodium silver salvarsan by aqueous picric acid, owing to the simultaneous precipitation of the diaminodihydroxyarsenobenzene as an insoluble picrate. From the solid products so obtained, the picrate is readily removed by acetone, leaving solids rich in silver chloride and silver oxide, respectively, but containing only a small amount of arsenic. Like Paal's colloidal silver, precipitated by acid from sols containing sodium protalbinat or lysalbinat (*Ber.*, 1902, **35**, 2224), these are insoluble in water but soluble in alkali.

In the case of sodium silver salvarsan, it is probable that colloidal silver is present as well as silver oxide, for a comparatively large amount of arsenic is not precipitated by picric acid, indicating that oxidation of the salvarsan by the silver oxide has occurred; whereas in the case of silver salvarsan the percentage of arsenic precipitated is the same as in the case of salvarsan alone. The oxidation products of salvarsan, 3-amino-4-hydroxyphenylarsenious oxide and the corresponding acid, are not precipitated by picric acid under these conditions.

The above results obtained with silver salvarsan and with sodium silver salvarsan, both in aqueous and alcoholic solution, seem to indicate conclusively that to the properties of diaminodihydroxyarsenobenzene and its salts as protective colloids must be ascribed the phenomena observed in their reactions with silver nitrate. In the case of silver salvarsan, silver chloride is formed by double decomposition and remains in solution, being protected by the diaminodihydroxyarsenobenzene dinitrate, but not essentially in stoichiometric proportions. In the case of sodium silver salvarsan, the silver is present as oxide and probably to some extent as metal, both again being protected by the colloidal sodium salvarsan as suggested by Raiziss and Gavron (*loc. cit.*), or by its hydrolytic product, "salvarsan base." The occurrence of some combination is not excluded by these results, but the double decomposition appears to form the predominating part of the reaction.

Contrary to the representation by Ehrlich and Karrer of the material obtained by them as a silver nitrate additive product, it follows that it is a mixture of two molecules of silver chloride and one of diaminodihydroxyarsenobenzene dinitrate; such a mixture would have the silver content observed by them. The precipitate obtained from this by Karrer (*Ber.*, 1919, **52**, 2323) on addition of sulphuric acid and considered by him to be a sulphate of the co-ordination compound is equally well explained as a mixture of

diaminodihydroxyarsenobenzene sulphate with two molecules of silver chloride.

With regard to the statement of Binz and Ludwig (*Ber.*, 1922, 55, [B], 3826), that oxidation occurs if more than one molecular proportion of silver nitrate be added to salvarsan, which does not, however, appear to arise out of the results described by them, no difference in the nature of the reaction in alcoholic solution was observed when one or two molecules were taken; in aqueous solution, oxidation did not occur when two molecules of silver nitrate were used.

Complete analyses of some specimens of commercial sodium silver salvarsan are given in the experimental part. It is seen that they differ from those made from salvarsan in containing sulphate instead of chloride. A specimen corresponding in composition to the commercial product, however, behaved in a similar manner to those described above when treated with picric acid and acetone.

EXPERIMENTAL.

*Isolation of Colloidal Silver Chloride from Methyl-alcoholic Silver Salvarsan Solutions.**—(a) *Two molecules of silver nitrate.* 246 Grams of silver nitrate were dissolved in 105 c.c. of dry methyl alcohol and added to a solution of 3 grams of salvarsan in 52 c.c. of methyl alcohol. The deep red solution obtained was added in a thin stream to 170 c.c. of dry ether. After shaking well, the granular precipitate was filtered, washed with ether, and dried in a vacuum desiccator (yield 2.3 grams). It formed a brown powder, soluble in water with the exception of a very slight residue, less soluble in methyl alcohol, soluble to a clear dark brown solution in aqueous sodium hydroxide (Found: Ag = 51.18; As = 10.04; N = 3.06; Cl = 15.47 per cent. Atomic ratio Ag:As = 7.1:2; N:As = 3.3:2; Cl:Ag = 0.9:1).

With regard to the nature of the arsenic compound present here together with silver chloride, the ratio of nitrogen to arsenic suggests that it partly consists of salvarsan nitrate (see p. 641). The remainder is probably salvarsan base, since the whole of the arsenic was present in the arseno-form, being precipitated from an aqueous solution of the substance by picric acid. One gram was dissolved in water, centrifuged clear from a trace of solid, and added to 100 c.c. of 1 per cent. aqueous picric acid, cooled in ice. The granular, brown product was filtered and dried (Found: Ag = 44.4; As = 8.61; Cl = 13.2 per cent. Ag:As = 7.17:2; Cl:Ag = 0.9:1). The filtrate contained no silver. The fact that the ratio of chlorine

* Throughout these experiments the air was displaced by nitrogen.

to silver is unchanged is additional evidence that the silver was present as silver chloride.

The alcohol-ether filtrate from the above precipitation by ether was poured into 690 c.c. of ether. 1.68 Grams of a lighter-coloured solid were obtained (Found: Ag = 3.71; Cl = 0.55; As = 27.16; N = 9.31. Ag : As = 0.19 : 2; N : As = 3.7 : 2. Salvarsan dinitrate made from the above salvarsan, mixed with 4.9 per cent. of silver chloride, requires As = 27.16 per cent.; N : As = 3.9 : 2).

(b) *One molecule of silver nitrate.* 1.08 Grams of silver nitrate were dissolved in 52 c.c. of methyl alcohol and added to 3 grams of salvarsan, dissolved in 52 c.c. of methyl alcohol. The clear red solution was added to 79 c.c. of dry ether cooled to 0°, and the precipitate filtered, washed with ether, and dried (yield 1.3 grams) (Found: Ag = 37.87; As = 16.19; Cl = 15.15 per cent. Ag : As = 3.25 : 2; Cl : Ag = 1.2 : 1). The ratio Ag : As is too high for a co-ordination compound, as before, and the ratio Cl : Ag shows the presence of silver chloride.

The filtrate was added to 1000 c.c. of ether. 2.1 Grams of solid were obtained, containing only a small quantity of silver, and arsenic corresponding to salvarsan dinitrate as before (Found: Ag = 5.65; As = 27.33 per cent.).

Isolation of Colloidal Silver Oxide from Methyl Alcoholic Sodium Silver Salvarsan Solution.—2.15 Grams of silver nitrate were dissolved in 105 c.c. of methyl alcohol and added to a mixture of 3 grams of salvarsan in 52 c.c. of methyl alcohol and 11.7 c.c. of 20 per cent. methyl-alcoholic sodium hydroxide. A solid separated, which was at first overlooked owing to its fineness of division and the intense colour of the solution; this was centrifuged off and dried in a vacuum (yield = 0.7 gram). It formed a black powder with metallic lustre, readily soluble in water to a clear dark brown solution, and effervescing slowly when treated with hydrazine hydrate (Found: Ag = 78.4; As = 5.1 per cent. Ag : As = 21.2 : 2).

Isolation of Colloidal Silver Chloride from Aqueous Silver Salvarsan Solution.—2.57 Grams of silver nitrate (2 mols.) were dissolved in 152 c.c. of water and added to 3.65 grams of salvarsan in 300 c.c. of water. The clear deep red solution formed was added to 6.2 grams of picric acid dissolved in 620 c.c. of water, and the precipitate washed by decantation and dried in a vacuum desiccator (yield 6.7 grams). It formed a brown powder (Found: Ag = 23.56; As = 14.70 per cent. Ag : As = 2.2 : 2). The filtrate contained no silver. From the above figures, 88.1 per cent. of the arsenic taken is present in the picric acid precipitate. This is in good agreement with the corresponding figure (86.5 per

cent.) for the precipitation of diaminodihydroxyarsenobenzene picrate alone (below); it follows that oxidation of the salvarsan by the silver nitrate had not occurred.

Extraction of the Picric Acid Precipitate with Acetone.—Two grams were shaken with 7.5 c.c. of acetone containing 5 per cent. of water. A large portion immediately dissolved, leaving a light yellow solid, which was centrifuged off, washed in the tube with another 7.5 c.c. of acetone, which was now only slightly coloured, and dried in a vacuum desiccator (yield 0.4 gram). It formed a faintly yellow powder (Found: Ag = 62.65; As = 3.47; Cl = 20.32. Ag:As = 25.1:2; Cl:Ag = 0.99:1; AgCl = 83.2 per cent.). On further washing with acetone, it tended to pass into colloidal solution.

Isolation of Colloidal Silver Oxide from Aqueous Sodium Silver Salvarsan Solution.—2.15 Grams of silver nitrate were dissolved in 12 c.c. of water and added to a solution of 3 grams of salvarsan in 65 c.c. of water and 3.4 c.c. of 45 per cent. sodium hydroxide. The clear dark solution was added to a solution of picric acid (excess), made by dissolving 9.2 grams of picric acid in 420 c.c. of hot water and cooling just before use. The mixture was well shaken and the granular precipitate washed and dried in a vacuum desiccator (yield 4.23 grams). It formed a dark solid, partly soluble in acetone (Found: Ag = 30.3; As = 13.9 per cent. Ag:As = 3.03:2. The ratio Ag:As in the quantities taken = 1:1). The filtrate contained no silver. The ratio of silver to arsenic is here increased to a markedly greater extent than in the corresponding precipitation of silver salvarsan (p. 639). This implies that part of the salvarsan has here been oxidised at the double bond by the silver oxide, since the oxidation products would not be precipitated, and it follows that the solid colloidal product obtained below partly consists of colloidal silver.

Extraction of the Picric Acid Precipitate with Acetone. Two grams were shaken with 7.5 c.c. of acetone, and the undissolved portion centrifuged off and washed twice by shaking with a similar quantity of acetone and centrifuging (yield 0.4 gram). It formed a black powder, insoluble in water but readily soluble in dilute alkali to a deep brown solution (Found: Ag = 84.92; As = 2.99; Cl = 1.28 per cent.). It caused slow effervescence in hydrazine hydrate, and therefore contained silver oxide; the presence of colloidal silver also is probable owing to the observed oxidation of the salvarsan. On further washing with acetone, it tended to pass into colloidal solution, but not so readily as the silver chloride (above).

3:3'-Diamino-4:4'-dihydroxyarsenobenzene Dipicrate.—One gram

of salvarsan was dissolved in 100 c.c. of water at 0° and treated with 100 c.c. of 1 per cent. aqueous picric acid solution at 0°. The suspension was shaken well and the granular precipitate washed by decantation and dried in a vacuum desiccator (yield, 86.5 per cent. of the theoretical). It forms a deep yellow powder, sparingly soluble in water, moderately soluble in ethyl alcohol, and readily soluble in methyl alcohol, or acetone containing a small quantity of water; m. p. 142° (corr.) with decomposition (Found: As = 18.6; N = 12.8. Atomic ratio N : As = 7.4 : 2. $C_{24}H_{18}O_{16}N_8As_2$ requires As = 18.2; N = 13.6 per cent. The ratio N : As in the salvarsan used, however, was 1.9 : 2, a number of specimens of salvarsan examined, which had been made by the usual commercial method, agreeing in this respect. A dipicrate made from this salvarsan requires N : As = 7.6 : 2).

3:3'-Diamino-4:4'-dihydroxyarsenobenzene Dinitrate.—1.96 Grams of salvarsan base, made by Christiansen's method (*J. Amer. Chem. Soc.*, 1921, **43**, 2207), were dissolved in 20 c.c. of dry methyl alcohol containing the theoretical quantity of nitric acid. The clear solution was poured into 400 c.c. of dry ether, and the solid obtained filtered, washed with ether, and dried in a vacuum desiccator (yield = 2.3 grams). It formed a pale yellow, granular solid, readily soluble in water, methyl alcohol, or ethyl alcohol, and decomposing on heating without melting (Found: As = 28.3; N = 10.35. N : As = 3.9 : 2. $C_{12}H_{12}O_2N_4As_2 \cdot 2HNO_3 \cdot 2H_2O$ requires As = 28.4; N = 10.6 per cent.). It was precipitated by dilute sulphuric and picric acids and, like salvarsan, gave an orange coloration with *p*-dimethylaminobenzaldehyde.

The Composition of Commercial Sodium Silver Salvarsan.

Specimens of the commercial product from three countries gave the following percentage results, corrected for loss of weight in a vacuum desiccator.

Speci- men.	Loss in a vacuum.	Ag.	As.	Na.	S (total).	S (sul- phate).	C.	H.	N.	Cl.
1	4.27	14.05	21.63	10.39	4.53	4.00	21.94	2.50	4.11	0.15
2	9.81	18.04	22.13	10.85	5.63	2.12	22.40	2.77	4.36	0.22
3	8.72	13.3	19.98	12.83	5.12	4.0	19.11	2.58	4.00	0.38

The Analytical Method Employed.

The method described by Binz, Bauer, and Hallstein (*Ber.*, 1920, **53**, [B], 426) was tried, but discarded in favour of the following, which was found to be more rapid and exact. 0.2 Gram of the substance is mixed in a flask with 2 grams of powdered potassium

permanganate and 10 c.c. of water. Ten c.c. of concentrated sulphuric acid are then gradually added and the mixture is warmed gently for fifteen minutes. Oxalic acid solution is next added until the colour is removed, and if silver is present this is now precipitated and removed as usual. The filtrate is evaporated to a volume of 60 c.c. and the arsenic estimated iodometrically.

If the substance to be examined is a picrate, it is necessary to remove completely the oxides of nitrogen resulting from the oxidation, otherwise the arsenic result may be slightly high. This is satisfactorily done by transferring the mixture to a beaker after the addition of oxalic acid, boiling gently for fifteen minutes, retransferring to the flask and diluting to 150 c.c. with water. The contents of the flask are now evaporated down to 60 c.c. and proceeded with as before. The figures marked with an asterisk in the following table are examples of the results obtained by this method:

Pure silver nitrate	Ag = 63.22, 63.05 (thiocyanate); 63.26*.
Silver salvarsan	Ag = 13.29; As = 20.04 (Carius); Ag = 13.24*; As = 19.55*.
" " another sample	As = 15.97 (Carius); 16.14*.
Picric acid precipitate (p. 639)	Ag = 30.28; As = 13.88 (Carius); Ag = 30.22*; As = 13.88*.

(Chlorine was estimated by the Carius method in all cases.)

In conclusion, the author would like to express his gratitude to Dr. T. A. Henry for his interest and valuable advice, and to Mr. W. Ramsay for assistance in the considerable amount of analytical work which has been involved.

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[Received, February 15th, 1923.]

LXXVII.—*Tesla-luminescence Spectra. Part I. The Form of Apparatus and the Spectrum of Benzene.*

By WILLIAM HAMILTON McVICKER, JOSEPH KENNETH MARSH, and ALFRED WALTER STEWART.

IN 1895, Wiedemann and Schmidt (*Ann. Physik*, 1895, 56, 20) showed that when electrical discharges from an induction coil were passed through the vapours of organic compounds at low pressures, a luminescence made its appearance. Later, Kauffmann (*Z. physikal. Chem.*, 1898, 26, 719; 27, 519; 1899, 28, 688; *Ber.*, 1900, 33, 1725) discovered that the vapours of certain organic compounds exhibited luminescence when influenced by the Tesla

discharge even when under ordinary pressure; and he endeavoured to trace a relationship between the colour and intensity of the luminescence on the one hand and the constitution of the substances under examination on the other. Kauffmann observed further that many substances which emitted a bluish-violet luminescence under the action of Tesla waves had also a power of fluorescing under the action of light.

These more or less qualitative investigations, although interesting, do not go to the root of the matter. Only an accurate investigation which includes both the visible and the ultra-violet spectrum can throw any real light on the problem as a whole; and up to the present this has not been attempted.*

In this and the following papers of the series the subject will be investigated over the whole photographic spectrum; and the influence of various factors—both constitutional and physical—will be examined.

The Apparatus.

The instrument used in this investigation was a Hilger quartz spectrograph, size C, which yields a photograph 200 mm. in length between the wave-lengths 2100 and 8000. The probable error in reading the plates dealt with in the present paper is about 1 unit at the ultra-violet end of the luminescence spectrum and 5 units at the red end; at least, independent readings are found to concord within these limits and are often closer.

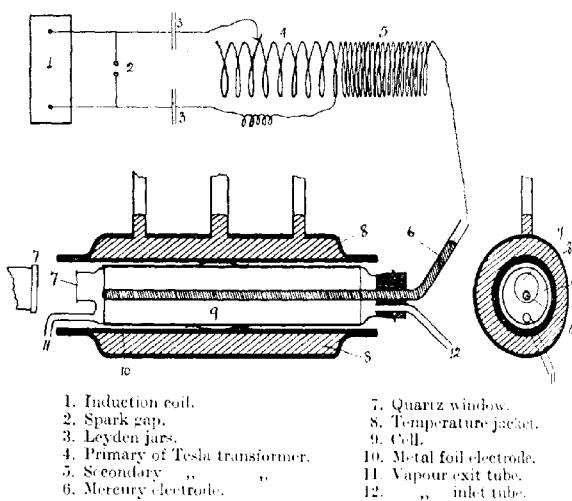
The cell in which the vapour was placed for examination (Fig. 1) was a glass tube about $1\frac{3}{4}$ inches in diameter, having at one end a quartz window of $\frac{3}{4}$ inch diameter. The other end of the tube was filled with a stopper through which passed a mercury electrode, enclosed in a glass tube. Two side-tubes blown into the main body of the cell served as inlet and outlet for the vapour under examination. The exterior of the cell was wrapped round with metallic foil, which constituted the exterior electrode. The quartz window of the cell was placed about 3 inches from the slit of the spectrograph.

Round the whole cell could be placed a steel jacket, into which three side-tubes were screwed. One of these served for introducing a thermometer; the other two were provided as inlet and outlet tubes for the vapour of a constant-boiling liquid. By this means, temperature regulation of the cell can be obtained. In actual practice hitherto, however, it has been sufficient to fill the jacket with mercury and heat it directly.

* Since this paper was sent in, Professor Victor Henri has informed us that he has independently been at work in this field, although he has not yet published any results.

In early experiments, the Tesla current was obtained from a laboratory-built Tesla transformer having forty coils in the primary (diameter 5 cm.) and 460 coils in the secondary (diameter 7.5 cm.), the whole being immersed in an insulation of heavy oil. A Leyden jar of about 1 litre capacity was used. This apparatus was worked with a choke-coil off a Clapp-Eastham quarter-kilowatt high-tension transformer, as supplied by Messrs. Hilger for use with their sector spectrophotometer. We obtained quite good results with this instrument; but it seemed advisable to employ a more powerful machine in order to be certain of getting the fullest possible spectra.

FIG. 1.



More recent work has therefore been done with a high-frequency apparatus supplied by the Medical Supply Association, Ltd. It contains 330 coils in its secondary (diameter 22 cm.), and its primary circuit is variable up to 30 coils. It is air-insulated and the secondary is directly coupled to the variable primary. Since one end of this instrument is permanently earthed, it is sufficient to connect the end of the high-tension secondary with the internal electrode of the cell and to earth either the steel jacket or the metal foil coating of the cell. In this way, a very steady Tesla discharge passes, as in an ozoniser, across the vapour which the cell contains. The Tesla transformer has four Leyden jars (capacity about 10 litres each).

connected in pairs on either side of the zinc spark-gap. As a source of current in this case, an 18-inch spark coil, supplied by X-Rays, Ltd., was employed.

It has been found that this arrangement produces the best results. The luminescence is, in the case of aniline, easily visible to the naked eye, being violet in tint. With a narrow slit in the spectrograph, the plate is well marked in fifteen minutes; and an exposure of one hour brings out the spectrum with perfect clearness. In order to avoid the influence of any stray light, all the exposures have been made in a darkened room.

The Tesla-luminescence Spectrum of Benzene.

In order to distinguish fluorescence spectra and absorption spectra from the spectra produced by the Tesla discharge, it seems desirable to coin a distinguishing word for the last-named group; and therefore the convenient name "Tesla-luminescence spectra" will be applied to them.

At ordinary pressures, aniline glows strongly under the Tesla discharge; but when the spectrum is photographed, it is found to be a short continuous spectrum lying approximately between the wave-numbers ($\nu = 1/\lambda$) 3333 and 2500, the brightest region being near 3076. Even with the most careful examination it shows no trace of either lines or bands. This spectrum appears with a 15-minute exposure; and increases in the exposure up to an hour led only to a slight extension of the spectrum at each end, unaccompanied by any change in character.

When benzene vapour is introduced into the cell at ordinary pressure and at its boiling point, it appears luminescent with a green glow; but on closer inspection this light emission seems to be produced by tiny green sparks; and some slight carbonisation of the benzene is noticeable. An attempt to photograph this "luminescence" yielded only a fragmentary carbon spectrum and some lines which were probably metallic and air lines produced by the sparking outside the cell at this pressure. The pressure in the cell was therefore reduced to 65 mm.; and under this pressure and at the ordinary temperature benzene emitted an easily photographable spectrum.

The Tesla-luminescence spectrum of benzene under these conditions is marked by a somewhat surprising regularity. It consists of a number of fine bands which, so far as we have observed them, fall into seven groups. The most refrangible band—that which occurs at $\nu = 3765$ —appears to belong to a band-group of which the remainder is concealed by the absorption of the benzene vapour

in the cell. Then follows a group of four strong bands * with a narrow band accompanying each; and two less strong and broader bands in which it seems probable that a primary and a secondary band may have been fused together. The bands of the series decrease in intensity more or less regularly from the more refrangible end. This system of ten bands may for convenience' sake be termed Group F.

This whole series of bands is repeated again in Groups E, D, and C. Of these, Groups E and D are the strongest. Following Group C at the least refrangible end are Groups B and A, where the bands are broad and more feeble. Beyond the least refrangible band of Group A there is an ill-defined region in which obviously some actinic effect has occurred on the plate; so that possibly there is another very feeble band-group here.

In Table I, in order to distinguish between the primary and secondary bands, the wave-numbers of the primary bands are given in full; whilst for the secondary bands only the last two figures are printed—the first two figures being the same as those of the primary *below*. All bands shown to the left of the full line in the table are of good definition, whilst bands to the right of the dotted line are exceedingly indistinct.

TABLE I.

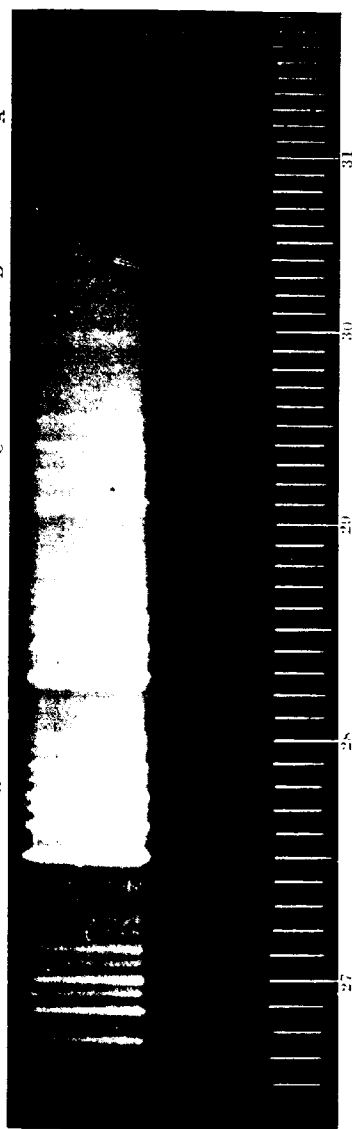
		1 Å							
Primary bands.		Group F.	Group E.	Group D.	Group C.	Group B.	Group A.		
Bright	Decreasing intensity ↓	1.	3752	3652	3554	3454	3357	3257	
			41	42	42	45	—	—	
		2.	3736	3636	3537	3438	3339	3242	
			25	25	28	28	—	—	
		3.	3717	3618	3521	3422	3322	3229	
			08	11	12	11	—	—	
		4.	3703	3602	3504	3405	3308	3211	
			93	92	98	—	—	—	
		5.	3686	3586	3488	3390	3294	3194	
			76	—	—	—	—	—	
Fainter	↓	6.	3765	3666	3570	3471	3376	3279	—

Inspection of these figures will bring out immediately one set of regularities in this spectral system which is exhibited by both the primary and the secondary bands alike. Taking any band in Group F, for example, there is a band corresponding to it in Group E and having a wave-number 99 units less on the average. For example,

* Towards the more refrangible end there appears to be a very faint line situated 2 Ångström units from the brightest line of the series: and this seems to be repeated in the other groups. These lines, however, are so faint that they have been omitted from the tables given later, as in these tables only absolutely certain data have been included.

BAND GROUPS.

G F E D C B A



The Tesla-luminescence spectrum of benzene.

(Note.—The scale is an approximate one of wave-lengths.)

the primary band 4 occurs in Group F at 3703 and in Group E at 3602, the difference being 101; the secondary band 4 in Group F occurs at 3693, and at 3592 in Group E, so that here again the difference is 101. The same relations hold good all down the series of the band-groups; so that, within experimental error, the following relationship holds between the wave-numbers of corresponding bands in the various Groups:

$$(F - E) = (E - D) = (D - C) = (C - B) = (B - A) = 99 \text{ approx.}$$

In addition to this simple regularity in the distribution of the corresponding members of the various band-groups throughout the Tesla-luminescence spectrum, there is another relationship which appears to be even more fundamental, since it connects together the whole of the bands of the spectrum.

The wave-numbers of all the bands appear to be expressible by the general formula

$$\nu = 98\cdot712 n - 98\cdot712 m/6 \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where n is successively made equal to 33, 34, 35 . . . and m in succession is put equal to 0, 1, 2, 3, 4 . . .

In the case of the primary bands, this formula is reducible to

$$\nu = 16\cdot452 l \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where l is an integer belonging to the series 194, 195, 196 . . . 228.

TABLE II.

Group F.		Group E.		Group D.	
Calc.	Obs.	Calc.	Obs.	Calc.	Obs.
3751.1	3752	3652.4	3652	3553.7	3554
34.6	36	35.9	36	37.2	37
18.2	17	19.5	18	20.7	21
01.7	03	03.0	02	04.3	04
3685.3	3686	3586.6	3586	3487.8	3488
68.8	66	70.1	70	71.4	71
Group C.		Group B.		Group A.	
3454.9	3454	3356.2	3357	3257.5	3257
38.5	38	39.7	39	41.0	42
22.0	22	22.9	22	24.6	29
05.6	05	06.8	08	08.1	11
3389.1	3390	3290.4	3294	3191.7	3194
72.7	76	73.9	79		

Table II shows the closeness in the agreement between calculated and observed values when formula (2) is employed. The figures which differ by more than 1.5 units from the calculated values are italicised. They are, without exception, those of very indistinct bands, in the cases of which the reading of the plates presented great difficulty. This difference of 1.5 units corresponds to about 1 Ångström unit in Group F and 1.5 Ångström units in Group A.

On the photographic plate it is represented by about 0.1 mm. Readings accurate within this limit cannot be expected, even in the most favourable circumstances.

The values of the secondary bands can be obtained by the use of the modified formula :

$$\nu = 16452 l - 11.$$

Tesla-luminescence and Fluorescence Spectra.

Since benzene was already known to emit a fluorescence spectrum, it seemed of interest to compare the results obtained in this field with those which have now been produced by means of the Tesla current. The two cases are not exactly comparable at present, since the fluorescence spectrum has been obtained from alcoholic solutions and not from benzene vapour like our Tesla-luminescence spectrum. We hope to examine the fluorescence of benzene vapour in the near future: but in the meantime it will be sufficient to direct attention to a striking point which comes to light when the fluorescence of benzene in alcoholic solution is compared with the Tesla-luminescence results.

Stark (*Physikal. Z.*, 1907, 8, 81, 250; *Ber.*, 1907, 40, 878) examined the fluorescence spectrum of benzene in 0.5 and 0.05 per cent. solutions. With the 0.05 per cent. solution he observed four bands with heads at 3676, 3571, 3534, and 3425. A more recent examination of the fluorescence spectrum of benzene by Dickson (*Z. wiss. Photographie*, 1912, 10, 166) led to the detection of bands at the wave-numbers 3848, 3795, 3733, 3631, 3537, 3436.

It is a well-established fact that the solvent exercises a definite influence on the optical properties of a solute. For example, Kauffmann and Beisswenger (*Ber.*, 1903, 36, 2494) observed that the colour of the fluorescence of dimethylnaphthearhodine changed according to the solvent employed, being green in ligroin, yellow in pyridine, orange-yellow in acetone, orange in ethyl alcohol, and reddish-orange in methyl alcohol. Again, in passing from vapour to solution in the case of benzene, it was found by Hartley (*Phil. Trans.*, 1908, [A], 208, 519) and Grebe (*Z. wiss. Photographie*, 1919, 9, 130) that absorption bands are shifted towards the less refrangible rays by 10–20 Ångström units. It seems reasonable to make a similar correction in the case of the fluorescence spectrum of benzene and to add 19 units to the wave-numbers given by Dickson for his bands. When the resulting figures are compared with those representing the brightest bands of the Tesla-luminescence spectrum in the same region, the following appears :

Wave-numbers of Tesla bands	3752	3632	3554	3454
Wave-numbers of fluorescence bands + 19	3752	3650	3556	3453

The agreement here is striking; and it is scarcely possible to avoid the inference that the two series of bands are directly related to each other in the closest fashion. It is evident that if the fluorescence spectrum be shifted bodily towards the more refrangible region it will fit, within experimental error, upon the principal portions of the Tesla-luminescence spectrum.

In this connexion it may be pointed out that the excitation by means of Tesla waves appears to bring out parts of the spectrum which are not easily stimulated by ordinary light; so that the Tesla method holds out great promise in this field. Further, since the fluorescence spectrum is included in the more complete Tesla-luminescence spectrum, it seems clear that both fluorescence and Tesla-luminescence must have some common factor in their origin; and the intricacies of the Tesla-spectra, with their exact and simple mathematical relationships, seem to offer a field of investigation much more promising than that which has hitherto been opened in the case of fluorescence excited by light-waves.

The Tesla-luminescence and Absorption Spectra of Benzene Vapour.

Striking as the foregoing comparison appears, a much more interesting problem arises when the Tesla-luminescence spectrum of benzene is placed side by side with the absorption spectrum of the same substance, both spectra being obtained with the substance in the gaseous state.

Hartley (*Phil. Trans.*, 1908, A, 208, 384) gives a map of the absorption bands detected by him in the vapour of benzene at a temperature of 100° and under a pressure varying from 206 mm. to 37 mm. In this map, he distinguishes the absorption bands as members of four different series, of which the first and second series are strong bands, whilst the third and fourth series contain weak bands.

When Hartley's first series of wave-numbers for the *absorption* bands is placed alongside the series of wave-numbers of the Tesla-luminescence *emission* bands in the same region, it is evident that the two series run side by side (see Table III). Further, if a constant difference of only two units be ascribed to a difference between his readings and ours, owing either to scale error or personal equation, then it is self-evident that the two series are identical within experimental error.

In drawing up the list of Hartley's absorption bands, we have confined ourselves to those bands which are actually marked on his map (*loc. cit.*, p. 484). This shows no bands at the positions marked with asterisks in Table III; but an examination of the fuller tables of bands given by Hartley in his text proves that there are actually regions of absorption corresponding to the Tesla-

luminescence spectrum even at these four points; so that the congruity between the two sets of measurements is even greater than appears from Table III. The bands have been taken in exactly the order in which they come in our Table I and in Hartley's spectrum-map, no band being omitted in either case.

TABLE III.

Hartley's absorption bands.	Hartley's values plus 2 units.	Tesla- lumin- escence emission bands.	Hartley's absorption bands.	Hartley's values plus 2 units.	Tesla- lumin- escence emission bands.
3761	3763	3765	3683	3685	3686
3754	3756	?	****	****	3676
3749—52	3751—54	3752	****	****	3666
3738	3740	3741	3656	3658	?
3734	3736	3736	3650	3652	3652
3722	3724	3725	****	****	3642
3716	3718	3717	****	****	3636
3708	3710	3708	3621	3623	3625
3700	3702	3703	3617—18	3619—20	3618
3691	3693	3693			

The interpretation of these results admits of no doubt. *The Tesla-luminescence spectrum of benzene vapour evidently represents the absorption spectrum reversed, just as the Fraunhofer dark line for sodium represents a reversal of the luminous D-line. Thus for the first time it has been possible to exhibit the Fraunhofer effect in the case of a complex organic compound of known constitution.*

In view of the simplicity of the benzene Tesla-luminescence spectrum, this achievement seems to mark the opening of a very promising chapter in spectroscopic work; and it suggests that after we have accumulated more experimental data, a mathematical treatment of absorption spectra may be taken up from an entirely fresh point of view.

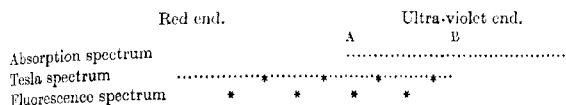
In this connexion, mention may be made of the following interesting relationship which has been detected by one of us (J.K.M.). The strongest band in the Tesla-luminescence spectrum of benzene is found at $\lambda = 2814$. Its wave-number = 3554, that is $6^3 \times 16.452$ (it has already been shown that the positions of the heads of the successive band-groups differ by 6 multiplied by the basic constant 16.452). Now calculation shows that a band with the wave-number $6^2 \times 16.452$ would have a wave-length = 1.68μ . This is exactly the position of a strong infra-red band in the benzene spectrum, of which the second octave, at 6.75μ , is also very strong (Coblentz, *Astrophys. J.*, 1904, 20, 207; *Pub. Carnegie Inst. Washington*, 1905, No. 35). Again, the value 6×16.452 would correspond to an infra-red band at 10.11μ ; and in actual practice, strong bands have been detected at 9.78μ and 10.30μ . At a distance

of 1.68 units from 10.11μ is found the band 11.80μ . The fundamental wave-length of the whole group would lie at 60.78μ .

General.

In the foregoing sections, only experimental results have been given. It seems advisable for the present not to theorise too much; but there are certain points which suggest themselves for discussion.

In the first place, it is evident that the Tesla-luminescence spectrum, the fluorescence spectrum, and the absorption spectrum of benzene are intimately related to one another in some way. Diagrammatically the relationship can be symbolised as shown below:



It will be noticed that the absorption and Tesla-luminescence spectra only overlap between A and B. This is due to the fact that Hartley did not examine the absorption spectrum in the region nearer the red end than A, and we are thus without data here. The disjointed fluorescence spectrum is indicated by asterisks; and asterisks in the Tesla-luminescence spectrum line show the corresponding bands in this spectrum.

The connexion symbolised above points to the existence of some factor common to all three phenomena. The substance benzene is, of course, common to all the experiments; but its part appears to be akin to that of a bell which gives out the same note when struck by any one of three hammers.

The points of most interest are two in number: (a) the relationship between the chemical structure of benzene and the vibrations which it emits or absorbs; and (b) the manner in which the benzene molecule is excited by light and by Tesla waves. To (a) we propose to return later in this series of papers when we have accumulated further evidence from other substances which we intend to examine. With regard to (b), two subdivisions of the problem are apparent: (1) Why do light vibrations and Tesla waves produce analogous effects on benzene? and (2) Is the light-emission which takes place under these actions due to the vibration of intact molecules or is it the result of molecular decomposition?

The analogy between the influence of Tesla waves and light-vibrations in this particular case is not difficult to see, since the Hertz waves are part of the same spectrum which contains light and X-rays. The only difficulty arises in connexion with the comparatively long wave-length of the Tesla vibrations. Lying, as

they do, far beyond the infra-red region of the spectrum, it might be supposed that their influence would be entirely molecular and that they would not interfere in the intricacies of intramolecular movement. This view, however, is obviously wrong, as can be shown by experimental evidence. Drude (*Z. physikal. Chem.*, 1897, 23, 267) proved that Hertz waves with a wave-length of 73 cm. were selectively absorbed by organic compounds containing hydroxyl groups; whence it is clear that the influence of Tesla vibrations extends to the most intimate structural peculiarities of molecules and is certainly not limited to the molecule as a whole.

Turning now to the second problem, the inquiry whether these three phenomena (absorption, fluorescence, Tesla-luminescence) are ascribable to the intact molecule or to a process of decomposition, the following facts appear to be available. In favour of the decomposition hypothesis there is certainly the evidence that at high pressures the passage of the Tesla discharge through an organic vapour produces a considerable amount of decomposition and also a rise in temperature. In the early experiments with aniline and acetone at ordinary pressure, quite a marked amount of carbon was deposited in the course of long exposures. On the other hand, at lower pressures the decomposition was much decreased, whilst the intensity of the luminescence was simultaneously increased—which seems to indicate that the two phenomena are not directly related. Further, the regularity of the spectrum exhibited by benzene at low pressures seems to militate against any decomposition hypothesis. This regularity implies a uniformity in the system which produces the spectrum. Now if the spectrum be that of benzene molecules in vibration, then its symmetry is easily admissible. But if it be assumed that it is a spectrum produced by the break-up of the benzene under the stress of the discharge, then it would be necessary to postulate an absolute regularity of decomposition which would be very hard to concede. The disintegration of a benzene molecule can be imagined to take place in various ways: by the formation of acetylene, by simple decomposition into carbon and hydrogen, etc.; and if the regularity of the Tesla-luminescence spectrum is to be accounted for, it would be necessary to assume that the benzene molecule was breaking down only in one particular manner, to the exclusion of all other modes of decomposition. This is scarcely a probable assumption. We hope, in the near future, to test the matter still further by an examination of the Tesla-luminescence spectrum of acetylene.

Again, unless it be assumed that the same decomposition is taking place in alcoholic solution, it is difficult to account for the fact that the Tesla-luminescence spectra and fluorescence spectra

show a marked relationship. The same is true of the absorption spectrum.

The weight of evidence, at present, seems mainly against the idea that the Tesla-luminescence spectrum arises in a decomposition of the molecule; but until further data have been accumulated the matter must be left in doubt.

In connexion with the theoretical side of these Tesla-luminescence spectra, it may be worth while to direct attention to a point which may turn out to be eventually of some importance. The Tesla-luminescence spectra provide us at last with the emission spectra of complicated compounds of known constitution; and the spectral series are evidently easily capable of mathematical treatment. It seems not beyond possibility that with the experience gained from a study of the Tesla spectra, the problem of the spectral series of the elements may be attacked from an entirely fresh point of view; and in this way a fresh line of investigation in atomic structure may be opened up.

On the purely experimental side, it appears that the electro-luminescence method provides an easy and convenient way of attacking the problem of fluorescence, owing to the fact that it reduces the necessary exposure to about a tenth of the period required when light is used as the exciting agent.

Summary.

1. The luminescence emitted by the vapours of various compounds when subjected to a Tesla discharge has been examined by means of a quartz spectrograph. At ordinary pressure and the boiling point, aniline emits a short, continuous spectrum, whilst benzene shows only a fragmentary carbon spectrum.

2. On reducing the pressure in the cell, benzene emits a spectrum containing a regular series of band-groups, each group having the same internal structure as the others.

3. When the bands of the fluorescence spectrum of benzene in alcoholic solution are compared with the Tesla-luminescence spectrum, it is found that by shifting the fluorescence spectrum bodily towards the ultra-violet through 19 units, it becomes identical with the brighter part of the Tesla-luminescence spectrum; and this shift of 19 units is in agreement with the values found by Hartley and by Grebe for the change produced in absorption spectra in passing from solution to vapour. This seems to establish a close relationship between Tesla-luminescence and fluorescence spectra.

4. When the bands of the Tesla-luminescence spectrum of benzene are compared with the absorption bands observed by Hartley in the spectrum of benzene vapour, it is found that the whole of Hart-

ley's strong absorption bands coincide in position with the Tesla-luminescence bands within experimental error. Thus the Tesla-luminescence presents an emission spectrum corresponding exactly to the absorption spectrum, and the Fraunhofer effect finds its parallel in this case of a complex chemical compound of known constitution.

5. The whole series of wave-numbers for the six primary series of the Tesla-luminescence bands can be expressed by means of a simple empirical formula, so that there can be no doubt that the bands actually constitute a single regular system.

6. When the formula is applied to the infra-red region, it gives results which are in agreement with experimental investigations previously made in this part of the benzene spectrum.

In conclusion, we wish to thank Professor Collic, F.R.S., Professor Smiles, O.B.E., F.R.S., and Dr. R. Wright for the interest they have taken in the work. The cost of part of the apparatus used was defrayed from the Heron Fund; and we wish to express our thanks to F. A. Heron, Esq., D.L., without whose assistance the apparatus could not have been purchased.

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[Received, January 19th, 1923.]

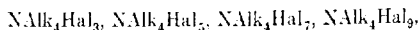
LXXVIII.- *Perhalides of Quaternary Ammonium Salts.*

By FREDERICK DANIEL CHATTAWAY and GEORGE HOYLE.

THE tetra-alkylammonium perhalides have been less fully investigated than the corresponding derivatives of ammonium and of the alkali metals. They are prepared very easily by adding the appropriate halogen, dissolved in alcohol or acetic acid, to a similar solution of the quaternary ammonium halide.

The present paper contains an account of a number of such compounds yielded by the tetramethyl-, tetraethyl-, and tetra-*n*-propylammonium halides.

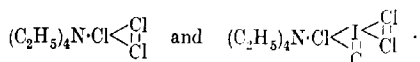
The composition of these compounds is represented by the general formulae :



and one example of a still higher form, $\text{NAlk}_4\text{Hal}_{13}$, appears to be produced when tetramethylammonium bromide is exposed to the action of bromine vapour in excess.

Concerning the mode of attachment of the halogens, we have

little or no knowledge. Almost all that can be said is that when they are heated halogen is liberated and a salt of the ammonium radicle is left, generally containing the halogen of least atomic weight. One halogen atom only appears to be united to the nitrogen, the others being attached to this or similarly to each other. Thus tetraethylammonium trichloride and tetraethylammonium tetrachloroiodide may be represented



Most of the tetra-alkyl perhalides can be recrystallised from alcohol, although in some cases a solution of the halogen has to be used as solvent.

Examples of each possible type of trihalide have been made including an example of a class hitherto unknown, the trichloride NAr_4Cl_3 . Many of the trihalides can be kept in a desiccator over lime for a considerable time with little appreciable decomposition, but some of the higher perhalides constantly, even if slowly, lose weight, whilst the odour of halogen is distinctly noticeable if they are kept in closed vessels.

EXPERIMENTAL.

Tetramethylammonium Dichlorobromide, $\text{N}(\text{CH}_3)_4\text{Cl}_2\text{Br}$.—Two grams of tetramethylammonium bromide were dissolved in the least possible quantity of acetic acid and the solution was cooled in a freezing mixture and saturated with chlorine. Bromine was at once set free, but as more chlorine was passed in, the colour of the solution changed from red to yellowish-green and *tetramethylammonium dichlorobromide* was deposited. It was recrystallised from warm acetic acid containing some dissolved chlorine, in which it is very soluble and from which it separates in pale yellow needles melting at 159° [Found: $\text{Cl} = 31.02$. $\text{N}(\text{CH}_3)_4\text{Cl}_2\text{Br}$ requires $\text{Cl} = 31.52$ per cent.].

Tetramethylammonium Chlorobromoiodide, $\text{N}(\text{CH}_3)_4\text{ClBrI}$.—Two grams of finely powdered iodine, suspended in a little glacial acetic acid, were converted into iodine monochloride by passing in a stream of chlorine, and to the solution thus obtained 2.5 grams of tetramethylammonium bromide, suspended in 10 c.c. of acetic acid, were added. The whole was warmed, filtered, and cooled, when *tetramethylammonium chlorobromoiodide* separated. It was recrystallised once from boiling alcohol, in which it is somewhat sparingly soluble, and from which it separates in small, twinned plates of a golden-yellow colour, m. p. 205° [Found: $\text{I} = 39.97$. $\text{N}(\text{CH}_3)_4\text{ClBrI}$ requires $\text{I} = 40.11$ per cent.].

Tetramethylammonium Tribromide, $N(CH_3)_4Br_3$.—Four grams of tetramethylammonium bromide were dissolved in the smallest possible quantity of a warm mixture of equal volumes of acetic acid and alcohol, and 4 grams of bromine were added. On cooling, *tetramethylammonium tribromide* separated. It was recrystallised from warm alcohol containing a little dissolved bromine, in which it is easily soluble and from which it crystallises in long, slender needles of a bright orange colour melting at 118.5° [Found : Br = 50.76. $N(CH_3)_4Br_3$ requires additional bromine = 50.92 per cent.].

In recrystallising the tribromide, it is necessary to use a solution of bromine in alcohol as solvent, as with alcohol alone there is considerable loss of halogen and the product which separates contains some reformed tetramethylammonium bromide.

Tetramethylammonium tribromide is able to unite with more bromine, but it has not been found possible to isolate a series of definite compounds.

A quantity of tetramethylammonium bromide was placed in a desiccator along with a small bottle containing liquid bromine. The solid rapidly absorbed a large amount of bromine and was converted first into the orange tribromide, which by further absorption of bromine was changed into a dark red oily liquid, then into a semi-solid mass, and finally into a hard, dark red solid, after which no further combination with bromine occurred.

0.6156 Gram of tetramethylammonium bromide absorbed 3.6520 grams of bromine, which nearly corresponds to the formation of a compound, $N(CH_3)_4Br_{13}$, which requires the addition of 3.833 grams of bromine. On exposing this product to the air, bromine vapour was given off abundantly and the same sequence of changes occurred in the reverse order until finally the more stable orange tribromide was left. When the latter was exposed in a vacuum over lime, it was found to lose weight only very slowly; for example, 0.1164 gram, after being kept in a vacuum over lime for fifty hours, had lost 0.0046 gram of bromine.

Tetramethylammonium Di-iodobromide, $N(CH_3)_4BrI_2$.—2.8 Grams of tetramethylammonium bromide were mixed with 4.6 grams of finely powdered iodine and dissolved in 40 c.c. of boiling alcohol. On cooling, *tetramethylammonium di-iodobromide* crystallised out. It was recrystallised twice from hot alcohol, in which it is easily soluble and from which it separates in short prisms of a dark crimson colour melting at 136° [Found : I = 62.32. $N(CH_3)_4BrI_2$ requires I = 62.23 per cent.]. The di-iodobromide was completely decomposed on being brought into contact with water with the formation of tetramethylammonium bromide and the tetraiodobromide described later.

Tetramethylammonium Tri-iodide, $N(CH_3)_4I_3$.—The melting point of tetramethylammonium tri-iodide, which is formed when tetramethylammonium iodide combines with two atoms of iodine, has been given as 110° (Weltzien, *Annalen*, 1856, **99**, 1) and 116° (Geuther, *ibid.*, 1887, **240**, 66).

A specimen obtained by the action of 4 grams of iodine on 3.1 grams of tetramethylammonium iodide and recrystallised twice from boiling alcohol, melted at 118° . It separated in short needles dark red by transmitted light and almost black with a brilliant violet, metallic lustre by reflected light [Found: additional iodine = 55.98. $N(CH_3)_4I_3$ requires additional iodine = 55.89 per cent.].

Tetramethylammonium Penta-iodide, $N(CH_3)_4I_5$.—The melting point of this compound has been given as 120° (Weltzien, *loc. cit.*), 126° and 127° (Silberrad and Smart, T., 1906, **89**, 174), 130° (Geuther, *loc. cit.*), and 131° (Stromh  lm, *J. pr. Chem.*, 1903, [ii], **67**, 345). A quantity was prepared by dissolving tetramethylammonium tri-iodide and the requisite amount of iodine in warm alcohol. It crystallised in very beautiful, thin, opaque plates with a brilliant green, metallic lustre and melted at 132° [Found: additional iodine = 71.40. $N(CH_3)_4I_5$ requires additional iodine = 71.63 per cent.].

An attempt was made to prepare tetramethylammonium hepta-iodide, at present unknown, by dissolving the additional amount of iodine and tetramethylammonium penta-iodide in alcohol. Dark green crystals of tetramethylammonium enneaiodide, $N(CH_3)_4I_9$, only were obtained. When the enneaiodide, mixed with the amount of tetramethylammonium iodide theoretically required to form the hepta-compound, was dissolved in warm alcohol, a product separated containing 78.21 per cent. of additional iodine [$N(CH_3)_4I_7$ requires additional iodine = 79.11 per cent.]. This, however, on recrystallisation from alcohol gave the penta-iodide and was probably a mixture of the penta- and the enneaiodides, as it melted at a low temperature.

Tetramethylammonium hepta-iodide seems therefore not to be formed under the conditions studied. The enneaiodide obtained as above described was recrystallised from warm alcohol which had been saturated with iodine at the ordinary temperature. It separated in opaque plates with a dark green, metallic lustre, less marked, however, than that of the penta-iodide, and melted at 109.5° (Geuther, *loc. cit.*, gives 110° ; Stromh  lm, *loc. cit.* 108°) [Found: additional iodine = 83.5. $N(CH_3)_4I_9$ requires additional iodine = 83.47 per cent.].

Tetramethylammonium Dibrom-iodide, $N(CH_3)_4Br_2I$.—Tetramethylammonium dibrom-iodide, which is one of the most stable of the perhalides, was obtained by the direct action of bromine on

tetramethylammonium iodide by Dobbin and Masson (P., 1886, 49, 846), who gave no analysis and stated the melting point to be 190° . It is more easily obtained by adding the equivalent amount of bromine, dissolved in about twice its bulk of glacial acetic acid, to tetramethylammonium iodide, suspended in about ten times its weight of alcohol, and warming till the solid dissolves. On cooling, tetramethylammonium dibromiodide is deposited. It is obtained pure after one recrystallisation from hot alcohol, in which it is readily soluble and from which it separates in small, needle-shaped crystals of a reddish-orange colour melting at 192° [Found: Br = 44.32. $N(CH_3)_4Br_2I$ requires Br = 44.29 per cent.].

Tetramethylammonium Tetraiodochloride, $N(CH_3)_4ClI_4$.—Two grams of tetramethylammonium chloride were mixed with 9.2 grams of iodine and dissolved in 60 c.c. of hot alcohol. On cooling, *tetramethylammonium tetraiodochloride* crystallised out. It was recrystallised from alcohol, in which it is sparingly soluble and from which it separates as opaque plates with a brilliant bluish-green, metallic lustre melting sharply at 110° [Found: I = 82.37. $N(CH_3)_4ClI_4$ requires I = 82.24 per cent.].

Tetramethylammonium Tetraiodobromide, $N(CH_3)_4BrI_4$.—3.1 Grams of tetramethylammonium bromide were mixed with 10.5 grams of iodine and dissolved in 100 c.c. of boiling alcohol. The hot solution was filtered and cooled, when *tetramethylammonium tetraiodobromide* crystallised out. It was recrystallised from boiling alcohol, in which it is sparingly soluble and from which it separates in almost opaque, rhombic plates with a brilliant dark green, metallic lustre melting at 124.5° [Found: I = 75.67. $N(CH_3)_4BrI_4$ requires I = 76.72 per cent.].

Tetramethylammonium Hexaiodobromide, $N(CH_3)_4BrI_6$.—Four grams of tetramethylammonium tetraiodobromide and 1.5 grams of iodine were dissolved in boiling alcohol which had been saturated with iodine at the ordinary temperature. On cooling, *tetramethylammonium hexaiodobromide* separated out in opaque plates with a dark green, metallic lustre similar in appearance to the tetraiodobromide, but possessing less lustre. It melted at 109° [Found: I = 83.27. $N(CH_3)_4BrI_6$ requires I = 83.17 per cent.].

Tetraethylammonium Trichloride, $N(C_2H_5)_3Cl_3$.—The action of chlorine on the tetra-alkylammonium chlorides is of especial interest as up to the present no perchlorides have been obtained. Neither ammonium chloride nor the chlorides of the alkali metals yield them under the conditions studied. A compound of this nature is, however, formed when a stream of chlorine is led over tetraethylammonium chloride.

The colourless salt absorbs chlorine, rapidly at first and after-

wards more slowly, becoming pale yellow, until a compound of the composition $N(C_2H_5)_4Cl_3$ is obtained. No further absorption of chlorine beyond this stage takes place at the ordinary temperature. The result of one typical experiment may be given: 1.5421 grams of tetraethylammonium chloride combined with 0.6596 gram of chlorine (Found: added chlorine = 29.95 per cent.). A small quantity was rapidly pressed between filter-paper and added to a solution of potassium iodide slightly acidified by acetic acid. The iodine which was liberated was then estimated by $N/10$ -solution of sodium thiosulphate [Found: added chlorine = 29.88. $N(C_2H_5)_4Cl_3$ required added chlorine = 29.98 per cent.].

Tetraethylammonium trichloride, thus obtained, is a crystalline powder of a bright yellow colour. It is very hygroscopic, smells strongly of chlorine, and melts at $42-45^\circ$ to a pale yellow liquid. It loses chlorine when exposed over lime and cannot be recrystallised without decomposition, but is perfectly stable when kept in a sealed vessel.

Chlorine also combines with tetramethylammonium chloride, without doubt forming a similar trichloride, but the absorption is much slower and the amount added to the dry salt at the ordinary temperature in the experiments which have been carried out never quite reached that required by the formula $N(CH_3)_4Cl_3$. The final product resembled tetraethylammonium trichloride, but was lighter in colour. In one experiment, for example, 0.48 gram of tetramethylammonium chloride absorbed 0.271 gram of chlorine, corresponding to 36.08 per cent. of added chlorine [$N(CH_3)_4Cl_3$ requires 39.29 per cent. of added chlorine].

Tetraethylammonium Dichlorobromide, $N(C_2H_5)_4Cl_2Br$.—Six grams of tetraethylammonium chloride were dissolved in the least possible quantity of warm acetic acid, 3 grams of bromine were added, and the liquid, after being strongly cooled, was saturated with chlorine. The red liquid quickly became pale green and *tetraethylammonium dichlorobromide* separated as a pale yellow solid. It was purified by dissolving in a little warm acetic acid, whereby some of the chlorine was lost and the red colour partly restored. On saturating the liquid with chlorine and cooling, the dichlorobromide separated in small, bright yellow needles melting at 69° [Found: $Cl = 25.55$. $N(C_2H_5)_4Cl_2Br$ requires $Cl = 25.24$ per cent.].

Tetraethylammonium di-iodochloride, $N(C_2H_5)_4ClI_2$.—3.5 Grams of tetraethylammonium chloride and 5.4 grams of iodine were dissolved in 45 c.c. of hot alcohol. On cooling, a mixture of tetraethylammonium di-iodochloride and tetraiodochloride separated. This was filtered off and the mother-liquor concentrated to a bulk of 20 c.c., filtered, and cooled, when *tetraethylammonium di-iodochloride*

separated alone in small plates of a crimson colour; m. p. 93° [Found: I = 60.41. $\text{N}(\text{C}_2\text{H}_5)_4\text{ClI}_2$ requires I = 60.51 per cent.]. It could not be recrystallised, as on dissolving in hot alcohol and cooling, a mixture of the di-iodochloride and tetraiodochloride was again obtained.

Tetraethylammonium Tetraiodochloride, $\text{N}(\text{C}_2\text{H}_5)_4\text{ClI}_4$.—3.2 Grams of tetraethylammonium chloride were mixed with 9.6 grams of iodine and dissolved in 40 c.c. of hot alcohol. On cooling, *tetraethylammonium tetraiodochloride* separated out. It was recrystallised twice from boiling alcohol, in which it is moderately soluble and from which it separates in shining plates brownish-red by transmitted light, with a dark blue metallic lustre by reflected light. It melts at 107.5° [Found: I = 75.21. $\text{N}(\text{C}_2\text{H}_5)_4\text{ClI}_4$ requires I = 75.40 per cent.].

Tetraethylammonium Hexabromochloride, $\text{N}(\text{C}_2\text{H}_5)_4\text{ClBr}_6$.—Tetraethylammonium chloride, when exposed in a desiccator alongside a small beaker containing an excess of bromine, rapidly absorbs the bromine, becoming first orange in colour, then red, and finally after a few days dark red, when no further increase in weight takes place. The product, which is a dark red, crystalline powder with a bluish tint, melts sharply at 53° and has a composition corresponding to the hexabromochloride of tetraethylammonium. The following is a typical analysis, all the other specimens obtained showing a composition approximating to this [Found: Br = 73.68. $\text{N}(\text{C}_2\text{H}_5)_4\text{ClBr}_6$ requires Br = 74.32 per cent.]. It only exists at the ordinary temperature under a considerable tension of bromine and cannot be recrystallised: when sealed up in a glass tube, it is stable, but bromine vapour can be recognised above the solid.

Tetraethylammonium Dibromochloride, $\text{N}(\text{C}_2\text{H}_5)_4\text{ClBr}_2$.—When tetraethylammonium hexabromochloride is exposed in a desiccator over lime, it loses bromine, rapidly at first, more slowly later, and becomes finally of a bright orange colour, after which further bromine is only very slowly given off. The compound thus obtained is a bright orange, crystalline powder melting at 79° [Found: Br = 48.84. $\text{N}(\text{C}_2\text{H}_5)_4\text{ClBr}_2$ requires Br = 49.11 per cent.].

A similar orange-coloured, crystalline substance separates on cooling a warm solution of tetraethylammonium chloride (1 mol.) in acetic acid containing the requisite amount of bromine (1 mol.). It cannot be separated and dried, however, without loss of bromine, and the dried product usually contains a quantity of bromine about 5 per cent. less than the theoretical. On exposing tetraethylammonium dibromochloride in a desiccator over lime, it loses bromine fairly rapidly at first, more slowly later, decomposition

proceeding finally at a very slow rate until tetraethylammonium chloride is left.

Tetraethylammonium Dichloriodide, $N(C_2H_5)_4Cl_2I$.—This compound was first prepared by Tilden (T., 1866, **19**, 145) and has since been obtained by several other chemists. Werner (T., 1906, **90**, 1625) gives the melting point as 98° . Zincke and Lawson (*Annalen*, 1887, **240**, 124), by acting upon tetraethylammonium chloride with hydrochloric acid and potassium iodate, obtained a substance which melted at 146 – 148° and gave off chlorine at 180° to which they assigned the same formula, $N(C_2H_5)_4Cl_2I$.

On adding tetraethylammonium chloride to a hydrochloric acid solution of an equivalent amount of iodine monochloride, a yellow, crystalline precipitate at once separated, which was filtered off and recrystallised twice from alcohol. It separated in shining, bright yellow plates, which melted sharply at 98° [Found: $I = 38.72$. $N(C_2H_5)_4Cl_2I$ requires $I = 38.66$ per cent.].

Tetraethylammonium Tetrachloriodide, $N(C_2H_5)_4Cl_4I$.—This compound separated as a yellow, crystalline powder when chlorine in excess was passed into a cold saturated solution of tetraethylammonium iodide in acetic acid. It was filtered off and dissolved in the least possible quantity of hot alcohol. On cooling, nothing separated, but on saturating the well-cooled solution with chlorine the tetrachloriodide crystallised out in a pure condition in small glittering plates of a bright yellow colour [Found: $I = 31.72$. $N(C_2H_5)_4Cl_4I$ requires $I = 31.81$ per cent.]. When heated, the compound did not melt sharply. It began to darken at about 130° and to liquefy at 155° , but fusion was not complete until a temperature of 173° had been reached, when a dark orange liquid which evolved bubbles of chlorine was formed.

The substance obtained by Zincke and Lawson must therefore have been, not tetraethylammonium dichloriodide, but impure tetraethylammonium tetrachloriodide.

Tetraethylammonium dibromiodide, $N(C_2H_5)_4Br_2I$, was obtained from tetraethylammonium iodide and bromine in exactly the same manner as the tetramethyl compound. It crystallises from alcohol in shining, rhombic plates of a deep, somewhat reddish-orange, colour and melts at 125° [Found: $Br = 38.45$. $N(C_2H_5)_4Br_2I$ requires $Br = 38.33$ per cent.].

Tetra-n-propylammonium chlorobromiodide, $N(C_3H_7)_4ClBrI$, was prepared in the same way as the corresponding tetramethyl compound. It crystallises in orange prisms, m. p. 143° [Found: $I = 29.17$. $N(C_3H_7)_4ClBrI$ requires $I = 29.61$ per cent.].

Tetra-n-propylammonium tetrachloriodide, $N(C_3H_7)_4Cl_4I$, separates in thin, bright yellow, glistening plates when chlorine is

passed into a cold solution of tetra-*n*-propylammonium iodide in alcohol. It was purified in the same manner as the corresponding ethyl compound. On being heated, it softens and melts with evolution of chlorine between 148° and 160° [Found: Cl = 31·21. $\text{N}(\text{C}_3\text{H}_7)_4\text{Cl}_4\text{I}$ requires Cl = 31·17 per cent.].

Tetra-n-propylammonium dichloriodide, $\text{N}(\text{C}_3\text{H}_7)_4\text{Cl}_2\text{I}$, was obtained in small, pale yellow needles on recrystallising the tetra-chloriodide from alcohol, the solution having been boiled for two minutes before it was filtered. It melts at 145° [Found: Cl = 18·36. $\text{N}(\text{C}_3\text{H}_7)_4\text{Cl}_2\text{I}$ requires Cl = 18·46 per cent.].

Tetra-n-propylammonium dibromiodide, $\text{N}(\text{C}_3\text{H}_7)_4\text{Br}_2\text{I}$, was prepared and purified in the same way as the corresponding methyl and ethyl compounds. It separates from hot alcohol in long, orange prisms melting at 140° [Found: Br = 34·01. $\text{N}(\text{C}_3\text{H}_7)_4\text{Br}_2\text{I}$ requires Br = 33·79 per cent.].

Tetra-n-propylammonium tri-iodide, $\text{N}(\text{C}_3\text{H}_7)_4\text{I}_3$, was obtained from iodine and tetra-*n*-propylammonium iodide in exactly the same manner as tetramethylammonium tri-iodide. It separates from alcohol in long, flattened needles of a dark crimson colour with a brilliant violet, metallic lustre by reflected light and orange-red by transmitted light. It melts sharply at 97° [Found: additional iodine = 45·14. $\text{N}(\text{C}_3\text{H}_7)_4\text{I}_3$ requires additional iodine = 44·76 per cent.].

Tetra-n-propylammonium penta-iodide, $\text{N}(\text{C}_3\text{H}_7)_4\text{I}_5$, was obtained by dissolving the requisite amount of iodine in a warm alcoholic solution of the tri-iodide. It was recrystallised twice from alcohol, from which it separates in shining, opaque plates with a very brilliant dark green, metallic lustre and melts at 82° [Found: additional I = 61·89. $\text{N}(\text{C}_3\text{H}_7)_4\text{I}_5$ requires additional I = 61·84 per cent.].

Tetra-n-propylammonium hepta-iodide, $\text{N}(\text{C}_3\text{H}_7)_4\text{I}_7$, was prepared by dissolving 5 grams of iodine in an alcoholic solution of 2 grams of tetra-*n*-propylammonium iodide. It was recrystallised from warm alcohol which had been saturated with iodine at the ordinary temperature and separated in small, almost opaque, plates with a dark blue, metallic lustre which melt at 85° [Found: additional I = 70·51. $\text{N}(\text{C}_3\text{H}_7)_4\text{I}_7$ requires additional I = 70·86 per cent.].

THE QUEEN'S COLLEGE,
OXFORD.

[Received, January 18th, 1923.]

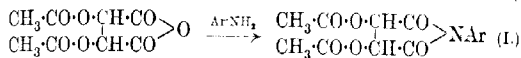
LXXIX.—*The Formation of Derivatives of Oxalacetic Acid from Tartaric Acid.*

By FREDERICK DANIEL CHATTAWAY and GEORGE DAVID PARKES.

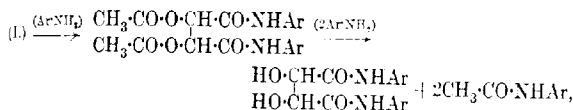
MANY years ago, Cohen and Harrison (T., 1897, 71, 1060) observed that very beautiful golden-yellow substances were formed when various aromatic amines were heated with diacetyltartaric anhydride. They were, however, produced in such small quantity that their constitution was not established.

A re-investigation of the reaction shows that they are arylimino-derivatives of oxalacetic acid of the general formula II.

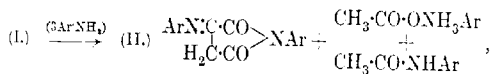
If certain precautions are taken, the action of primary aromatic amines upon diacetyltartaric anhydride follows a perfectly normal course. The first product of the reaction is a diacetyltartranil (I) :



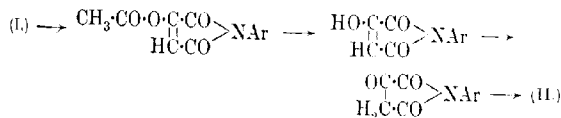
This, under the further action of the base, forms chiefly the normal diacetyltartranilide or its decomposition products, a tartranilide and an acetanilide,



whilst in a subordinate degree an arylimino-derivative of oxalacetic acid together with an acetanilide is produced,



the reaction probably proceeding somewhat as follows :



EXPERIMENTAL.

Diacetyltartaric anhydride is best prepared by adding a slight excess (3.5 mols.) of acetic anhydride and a few drops of strong sulphuric acid to dry powdered tartaric acid (1 mol.). The mixture on shaking or stirring becomes warm, the tartaric acid dissolves,

and, on cooling, diacetyltartaric anhydride separates. On filtering by the aid of the pump, washing with a little benzene, and drying for a few minutes at 100° , an almost theoretical yield of diacetyltartaric anhydride is obtained in a condition sufficiently pure for ordinary use. From this a yield of 90 per cent. of the theoretical of pure diacetyltartaric anhydride, m. p. 135° , can be obtained by recrystallisation from benzene.

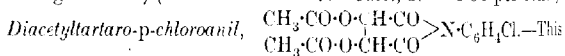
Preparation of Anils of Diacetyltartaric Anhydride.

From the behaviour of other anhydrides of dibasic acids, it might be expected that diacetyltartaric anhydride would react with primary arylamines to form anils, water being eliminated. This has been found to be the case, the anil in every instance being formed when equivalent amounts of the anhydride and the arylamine are melted together and the mixture kept in a state of fusion for a few minutes. A viscid solid mass is left on cooling, from which the anil can be isolated, although in some cases with difficulty.

Diacetyltartranil has been prepared by Vallée (*Ann. Chim. Phys.*, 1908, [iii], 15, 331) by heating together at 135° diacetyltartaric anhydride and diphenylcarbamide.

It can be obtained more easily by heating together equivalent amounts of diacetyltartaric anhydride and aniline, keeping the mixture just above the point of fusion (that is, at about 110°) for four to five minutes. On cooling, a dark red resin-like mass is obtained which dissolves readily in boiling alcohol. From this solution, on cooling and vigorously shaking, the anil separates as a white, crystalline solid. It is necessary to avoid any excess either of aniline or of anhydride, as otherwise the product is very difficult to crystallise.

Diacetyltartranil separates from boiling alcohol, in which it is readily soluble, in colourless, flattened needles which melt at 125.5° (Vallée gives 124°) (Found: N = 4.79. Calc., N = 4.81 per cent.).



and the other anils described below were prepared and isolated exactly as described above. It crystallises from boiling alcohol, in which it is somewhat sparingly soluble, in colourless needles, m. p. 173° . It has $[\alpha]_D^{20} + 106.86^{\circ}$ in acetone ($l = 2$, $c = 2.84$) (Found: Cl = 11.08. $\text{C}_{14}\text{H}_{12}\text{O}_6\text{NCl}$ requires Cl = 10.89 per cent.).

Diacetyltartaro-p-bromoanil crystallises from boiling alcohol, in which it is sparingly soluble, in colourless needles, m. p. 184° . It has $[\alpha]_D^{20} + 81.58^{\circ}$ in acetone ($l = 2$, $c = 0.95$) (Found: Br = 21.26. $\text{C}_{14}\text{H}_{12}\text{O}_6\text{NBr}$ requires Br = 21.59 per cent.).

Diacetyltartaro-2:4-dichloroanil crystallises from boiling alcohol,

in which it is readily soluble, in small, colourless needles, m. p. 138°. It has $[\alpha]_D^{20} + 63.02^\circ$ in acetone ($l = 2$, $c = 2.396$) (Found: $Cl = 19.8$. $C_{14}H_{11}O_6NCl_2$ requires $Cl = 19.70$ per cent.).

Diacetyltartaro-2:4-dibromoanil crystallises from boiling alcohol, in which it is readily soluble, in colourless needles, m. p. 172°. It has $[\alpha]_D^{20} + 58.01^\circ$ in acetone ($l = 2$, $c = 2.55$) (Found: $Br = 35.5$. $C_{14}H_{11}O_6NBr_2$ requires $Br = 35.60$ per cent.).

Diacetyltartaro-o-toluil crystallises from boiling alcohol, in which it is readily soluble, in small, colourless needles, m. p. 128°. It has $[\alpha]_D^{20} + 99.42^\circ$ in acetone ($l = 2$, $c = 2.062$) (Found: $N = 4.50$. $C_{15}H_{13}O_6N$ requires $N = 4.60$ per cent.).

Diacetyltartaro-m-toluil crystallises from boiling alcohol, in which it is moderately easily soluble, in very small, colourless needles, m. p. 146°, and $[\alpha]_D^{20} + 112.04^\circ$ in acetone ($l = 2$, $c = 0.54$) (Found: $N = 4.52$. $C_{15}H_{13}O_6N$ requires $N = 4.60$ per cent.).

Diacetyltartaro-p-toluil crystallises from boiling alcohol, in which it is easily soluble, in small, colourless needles, m. p. 127°. It has $[\alpha]_D^{20} + 118.54^\circ$ in acetone ($l = 2$, $c = 1.316$) (Found: $N = 4.56$. $C_{15}H_{13}O_6N$ requires $N = 4.60$ per cent.).

Diacetyltartaro-2:4-xylil crystallises from boiling alcohol, in which it is fairly easily soluble, in colourless needles, m. p. 118.5°, and $[\alpha]_D^{20} + 166.4^\circ$ in acetone ($l = 2$, $c = 0.88$) (Found: $N = 4.23$. $C_{16}H_{15}O_6N$ requires $N = 4.37$ per cent.).

Diacetyltartaro-3-naphthil crystallises from boiling alcohol, in which it is sparingly soluble, in colourless needles, m. p. 166°, and $[\alpha]_D^{20} + 134.6^\circ$ in acetone ($l = 2$, $c = 0.572$) (Found: $N = 4.07$. $C_{18}H_{15}O_6N$ requires $N = 4.10$ per cent.).

Action of Excess of Aniline upon Diacetyltartaric Anhydride.

It has been pointed out already in describing the preparation of tartranils that it is much more difficult to isolate the anil if excess of either reacting constituent is present.

When a slight excess of aniline is used, the product, when dissolved in alcohol, gives a yellow solution, and the anil which separates is coloured by a yellow impurity. This yellow colour becomes more marked as the amount of aniline is increased and when a considerable excess of aniline is employed a bright yellow solid product is formed. This contains in addition to acetanilide and tartranilide the compound of a bright yellow colour described by Cohen and Harrison (*loc. cit.*), which was isolated as follows by a method similar to that described by them.

A mixture of 34 grams of aniline and 40 grams of diacetyltartaric anhydride was heated in an oil-bath to 150°, at which temperature it was completely liquid. As the heating was continued, the mass

became more and more viscous and finally, after about forty-five minutes, solidified to a bright yellow mass. It was found of no advantage to heat for a longer period or to a higher temperature, or to use a larger proportion of aniline, as the subsequent isolation of the yellow compound was thereby rendered more difficult and the yield was not increased.

The yellow solid mass was extracted several times with boiling alcohol, when a dark yellowish-brown solution resulted, which on cooling deposited a considerable quantity of what appeared to be a single, bright yellow substance but which was actually a mixture of a considerable quantity of a white substance, coloured intensely by a small quantity of a yellow compound. This yellow mixture was filtered off and dried. The dark coloured alcoholic mother-liquor deposited, on dilution with water, a mixture of acetanilide and the excess of aniline used.

The yellow solid, after being dried and finely powdered, was extracted with benzene in a Soxhlet apparatus until the solution which siphoned over was almost colourless. The benzene solution in the flask was of a deep reddish-orange colour, and on cooling deposited a bright yellow substance, which, when filtered off and dried, formed a considerable bulk of a fluffy, crystalline powder.

The residue in the Soxhlet thimble was almost colourless. It was recrystallised from alcohol, in which it was very sparingly soluble and from which it separated as a felted mass of fine, white needles which melted at 264° . It seemed likely, therefore, to be tartranilide, which melts at this temperature (Found: $N = 9.37$. Tartranilide, $C_{16}H_{16}O_2N_2$, requires $N = 9.34$ per cent.). Its properties were compared with those of a small quantity of tartranilide, prepared by Frankland and Slaton's method (T., 1903, 83, 1349), and found to agree with those of the latter in every particular.

An exactly similar mixture of tartranilide, acetanilide, and the yellow compound is obtained when aniline is similarly heated with diacetyltartranil and can be separated into its constituents as described above, but this method offers no advantage over the direct preparation from diacetyltartaric anhydride.

The yellow substance isolated by means of the Soxhlet extraction was twice recrystallised from benzene, then once from acetone and again once from benzene. A yield of from 1 to 2 per cent. of the weight of the diacetyltartaric anhydride used was obtained. In a large number of experiments, this yield was only occasionally and slightly exceeded, and the yellow compound appears to be produced as a by-product.

It is moderately soluble in boiling alcohol or benzene, more so in glacial acetic acid or acetone, and insoluble in water. It melts

at 232°. It does not react with acetic anhydride. Heated with excess of bromine, it decomposes and *s*-tribromoaniline is formed (Found: C = 72.89; H = 4.54; N = 10.53, corresponding with an empirical formula C_6H_6ON , which requires C = 72.90; H = 4.55; N = 10.60 per cent.).

Since the compound is obtained either from diacetyltartaric anhydride or from diacetyltartranil by simply heating to a moderate temperature with aniline, and as it is unlikely that the chain of four carbon atoms in the tartaric residue is broken during the reaction, the compound must contain at least ten carbon atoms in its molecule, and its molecular formula must accordingly be double the empirical formula, that is, $C_{16}H_{12}O_2N_2$. This was confirmed by a determination of the molecular weight by the depression of the freezing point of benzene (Found: $M = 261.1$. $C_{16}H_{12}O_2N_2$ requires $M = 264.2$).

From the circumstance that acetanilide is formed in the reaction, as is also tartranilide, it is evident that the acetyl groups of the anhydride are removed by the aniline.

These facts, together with the mode of formation and the molecular composition, show that the yellow compound must be a derivative of oxalacetic acid and have the constitution represented by the formula

$$\begin{array}{c} C_6H_5 \cdot N : C \cdot CO \\ H_3C \cdot CO \end{array} > N \cdot C_6H_5 \cdot *$$

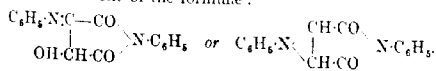
To complete the identification of the compound, it was compared with a specimen of phenyliminosuccinil† prepared from oxalacetic ester by the method of Wislicenus and Spiro (*Ber.*, 1889, 22, 3348) and found to be identical with it in every respect.

p-Tolyliminosuccino-*p*-toluil, $\begin{array}{c} C_6H_4Me \cdot N : C \cdot CO \\ H \cdot CO \end{array} > N \cdot C_6H_4Me$. As the

formation of derivatives of oxalacetic acid from tartaric acid is of considerable interest, a series of these anils has been prepared by his method, which appears to be a general one.

Ten grams (1 mol.) of diacetyltartaric anhydride and 20 grams † mols.) of *p*-toluidine were heated together at 150° for about

* Cohen and Harrison (*loc. cit.*) suggested that the compound would probably be found to have one of the formulae:

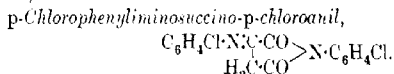


† This and the other similarly constituted compounds described in this paper and formed by the replacement of the ketonic oxygen of oxalacetic acid by an arylimino-group, just as benzylideneaniline is obtained from benzaldehyde, are described as iminosuccinils to conform to the accepted system of nomenclature which regards them as derived from the corresponding pyridogen and not oxo-compounds.

fifteen minutes until the viscid mixture solidified to a bright yellow mass. This was allowed to cool and extracted several times with boiling alcohol. On cooling, a bright yellow solid separated, which was filtered off, powdered, washed with dilute hydrochloric acid to remove excess of *p*-toluidine, dried, and extracted with benzene in a Soxhlet apparatus. On cooling, the benzene solution deposited small crystals of a bright yellow colour which were recrystallised from benzene, then from acetone, and again from benzene.

p-Tolyliminosuccino-*p*-toluid is moderately easily soluble in boiling benzene, from which it separates in thin golden-yellow plates. It melts at 237° (Found: C = 73.75; H = 5.37; N = 9.58. $C_{18}H_{16}O_2N_2$ requires C = 73.9; H = 5.47; N = 9.58 per cent.).

m-Tolyliminosuccino-*m*-toluid was prepared similarly to its *p*-isomeride, but it was found necessary to heat the mixture at 150° for two hours, the reaction apparently taking place much more slowly in this case. Its isolation also was more difficult, since tartarodi-*m*-toluidide, which is the main product of the reaction, and the bulk of which remains in the Soxhlet apparatus, is yet somewhat soluble in benzene, and could only be removed from the benzene solution by repeatedly allowing it to crystallise out; the mother-liquor from each crop of crystals being evaporated to dryness and again fractionally crystallised from benzene. *m*-Tolyliminosuccino-*m*-toluid separates from boiling benzene, in which it is easily soluble, in minute, bright yellow needles which melt at 162° (Found: N = 9.44. $C_{18}H_{16}O_2N_2$ requires N = 9.58 per cent.).



—This, like the corresponding bromo-compound, was prepared and isolated by the method already described, with but slight necessary modifications.

p-Chlorophenyliminosuccino-*p*-chloroanil separates from boiling benzene or acetone, in both of which it is moderately easily soluble, in small, thin, irregular plates of a bright yellow colour. It melts at 245° (Found: Cl = 21.68. $C_{16}H_{10}O_2N_2Cl_2$ requires Cl = 21.30 per cent.). It is also formed when *p*-chloroaniline is heated with diacetyl tartaro-*p*-chloroanil.

p-Bromophenyliminosuccino-*p*-bromoanil resembles closely the corresponding chloro-compound. It is moderately easily soluble in boiling benzene, from which it crystallises in small, thin, bright yellow, irregular plates, which when dry form a fluffy, crystalline powder. It melts at 260° (Found: Br = 37.71. $C_{16}H_{10}O_2N_2Br_2$ requires Br = 37.8 per cent.).

p-Chlorophenyliminosuccinil, $\begin{matrix} \text{C}_6\text{H}_4\text{Cl}\cdot\text{N}\cdot\text{C}\cdot\text{CO} \\ \text{H}_2\text{C}\cdot\text{CO} \end{matrix} > \text{N}\cdot\text{C}_6\text{H}_5$.—As an iminosuccinil is produced very easily by heating any arylamine (3 mols.) with any diacetyltartril, mixed derivatives can be obtained. Thus the action of *p*-chloroaniline on diacetyltartril gives rise to *p*-chlorophenyliminosuccinil. This compound is sparingly soluble in boiling benzene, from which it separates in minute, thin, irregular plates of a bright yellow colour. It melts at 268° (Found: Cl = 11.80. $\text{C}_{16}\text{H}_{11}\text{O}_2\text{N}_2\text{Cl}$ requires Cl = 11.90 per cent.).

Phenyliminosuccino-*p*-chloroanil, $\begin{matrix} \text{C}_6\text{H}_5\cdot\text{N}\cdot\text{C}\cdot\text{CO} \\ \text{H}_2\text{C}\cdot\text{CO} \end{matrix} > \text{N}\cdot\text{C}_6\text{H}_4\text{Cl}$, was similarly obtained by heating aniline with diacetyltartaro-*p*-chloroanil. It resembles its isomeride closely, but is of a slightly different shade of yellow and is much more readily soluble in benzene. It separates from boiling benzene in minute, thin, irregular plates of a bright yellow colour and melts at 244° (Found: Cl = 11.78. $\text{C}_{16}\text{H}_{11}\text{O}_2\text{N}_2\text{Cl}$ requires Cl = 11.90 per cent.).

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[Received, January 22nd, 1923.]

LXXX.—*The Higher Oxide of Nickel.*

By OWEN RHYS HOWELL.

CONSIDERABLE attention has been directed to the precipitation of nickel by means of alkali and an oxidising agent (Bayley, *Chem. News*, 1879, 39, 81; Carnot, *Compt. rend.*, 1889, 108, 610; Schröder, *Chem. Zentr.*, 1890, i, 931; Bellucci and Clavari, *Gazzetta*, 1905, 14, ii, 234; *Atti R. Accad. Lincei*, 1905, [v], 14, ii, 234; *ibid.*, 1907, [v], 16, i, 647; Pellini and Meneghini, *Z. anorg. Chem.*, 1908, 60, 178; Tanatar, *Ber.*, 1909, 42, 1516; Turbandt and Riedel, *ibid.*, 1911, 44, 2565; *Z. anorg. Chem.*, 1911, 72, 219), but the reaction has not been investigated quantitatively and the nature of the precipitate does not appear to have been satisfactorily established. The matter has therefore been examined by precipitating nickel sulphate solution with sodium hydroxide and sodium hypochlorite, and also with lime and bleaching powder in a manner similar to that adopted in the case of cobalt (this vol., p. 65).

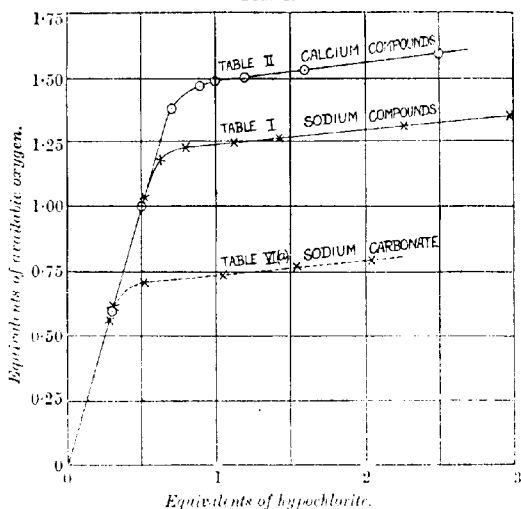
EXPERIMENTAL.

Materials.—The nickel sulphate was free from iron and contained only a trace of cobalt. The hypochlorite solutions were made as already described (*loc. cit.*).

Method of Investigation.—The nickel sulphate solution was precipitated with a solution containing the requisite amounts of alkali and hypochlorite, and the resulting precipitate analysed. The mode of procedure and methods of analysis were the same as in the case of cobalt (*loc. cit.*). All the quantities are expressed as equivalents per equivalent of nickel taken for precipitation.

It was found, as stated by Bellucci and Clavari (*loc. cit.*), that the precipitate was extremely unstable and rapidly lost oxygen even in suspension at the ordinary temperature. In order to obtain strictly comparable results, care was therefore taken that

FIG. 1.



the time between precipitation and analysis of the precipitate was exactly the same in any series of experiments.

Action of Hypochlorite Alone.—Sodium hypochlorite free from alkali does not react immediately with nickel sulphate solution at the ordinary temperature; some time elapses before the reaction begins. As in the case of cobalt, a black precipitate of the higher oxide is obtained with evolution of chlorine, but the precipitation is so incomplete and so slow compared with the action in the presence of alkali that it has not been studied in detail.

Action of Hypochlorite in presence of Alkali.—A constant excess of alkali was used with varying amounts of hypochlorite. The precipitate was stirred for an hour, allowed to settle over-night,

and filtered; samples of the solid were taken for analysis. The results obtained with the sodium compounds are given in Table I and those with the calcium compounds in Table II. The values are plotted in Fig. 1.

TABLE I.

NaOH.	Na ₂ CO ₃	Total alkali.	NaOCl.	Available oxygen.
2.020	0.020	2.040	0.312	0.622
2.012	0.024	2.036	0.524	1.037
2.014	0.020	2.034	0.624	1.180
2.014	0.024	2.038	0.800	1.225
2.014	0.024	2.038	1.122	1.241
2.014	0.024	2.038	1.420	1.260
2.018	0.026	2.044	2.260	1.308
2.018	0.028	2.046	2.980	1.350

TABLE II.

Ca(OH) ₂ .	Ca(OCl) ₂ .	Available oxygen.	Ca(OH) ₂ .	Ca(OCl) ₂ .	Available oxygen.
1.806	0.300	0.598	1.806	1.000	1.483
1.800	0.500	1.000	1.810	1.200	1.501
1.810	0.700	1.375	1.810	1.600	1.528
1.806	0.900	1.465	1.810	2.500	1.593

It is seen that the action of the hypochlorite in oxidising the precipitated hydroxide is quantitative up to the addition of half an equivalent (sesquioxide stage) and further while peroxidation occurs. The extent of the peroxidation is greater with the calcium compounds than with the sodium compounds, probably because the reaction is more rapid owing to the formation of the comparatively insoluble calcium sulphate. The peroxidised precipitate catalytically decomposes the hypochlorite, consequently the use of larger amounts of hypochlorite results in only a small, but proportionate, increase in the oxygen content.

Action of Alkali.—A constant amount of hypochlorite was used with varying amounts of alkali. Two series of experiments were made; in (a) the suspension was stirred for half an hour after precipitation and an aliquot part taken for analysis; in (b) the suspension was stirred for two hours, allowed to settle over-night, filtered, and the solid analysed. The results obtained with the sodium compounds are given in Tables III (a) and III (b) and with the calcium compounds in Tables IV (a) and IV (b), respectively. The values are plotted in Fig. 2.

TABLE III (a).

NaOH.	Na ₂ CO ₃ .	Total alkali.	NaOCl.	Available oxygen.
0.448	0.014	0.462	1.418	0.460
0.709	0.021	0.730	1.424	0.732
0.968	0.032	1.000	1.418	0.990
1.166	0.034	1.200	1.424	1.182
1.474	0.042	1.516	1.424	1.268
2.406	0.032	2.438	1.418	1.278

TABLE III (b).

0.443	0.044	0.487	1.421	0.424
0.958	0.032	0.990	1.405	0.838
1.203	0.030	1.233	1.418	1.035
1.406	0.022	1.428	1.421	1.202
1.629	0.026	1.655	1.421	1.255
1.846	0.020	1.866	1.421	1.260
2.682	0.020	2.702	1.438	1.272

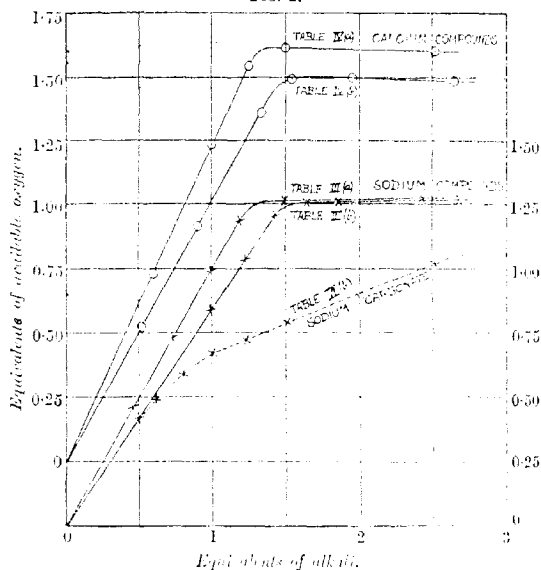
TABLE IV (a).

$\text{Ca}(\text{OH})_2$	$\text{Ca}(\text{OCl})_2$	Available oxygen.	$\text{Ca}(\text{OH})_2$	$\text{Ca}(\text{OCl})_2$	Available oxygen.
0.600	1.200	0.732	0.520	1.212	0.525
1.000	"	1.232	0.908	1.200	0.916
1.250	"	1.540	1.342	1.200	1.360
1.500	"	1.610	1.550	1.208	1.498
2.520	"	1.605	1.960	1.210	1.496

TABLE IV (b).

2.658	1.200	1.482
3.780	1.208	1.459
5.052	1.204	1.418

FIG. 2.



It is seen that the curves pass through the origin, showing that the direct action of the hypochlorite is negligibly slow compared with that of the alkali. In all cases the values in series (b) are less than the corresponding values in series (a) owing to the greater

decomposition of the peroxide during the greater interval between precipitation and analysis. Although precipitation is complete at one equivalent of alkali, the curves do not exhibit a break at this point; the decomposition of the precipitate is retarded by alkali, and for this reason there is an increase in the available oxygen with excess of alkali.

The loss of oxygen by the precipitate and its retardation by alkali will be evident from Table V. Precipitation was made in A with one equivalent of alkali and in B with one and a half equivalents, other conditions being identical. The suspensions were allowed to stand and the available oxygen was determined at intervals. It is evident that the decomposition in the presence of half an equivalent of alkali is far slower than in the neutral solution. It is also seen that, as stated by Bellucci and Clavari (*loc. cit.*), the decomposition proceeds with no arrest at the sesquioxide stage.

TABLE V.

The precipitating solution was 1 equiv. of NaOH and 1 equiv. of NaOCl in A and 1.5 equivs. of NaOH and 1 equiv. of NaOCl in B.

Time of standing.	Available oxygen.		Time of standing.	Available oxygen.	
	A.	B.		A.	B.
0.5 hours	1.137	1.242	5 days	0.879	1.136
8 "	0.990	1.212	7 "	0.833	1.124
24 "	0.976	1.203	2 months	0.761	0.989
2 days	0.932	1.186	4 "	0.713	0.940
3 "	0.914	1.160	6 "	0.684	0.870
4 "	0.897	1.146			

Action of Sodium Carbonate.—The precipitating solutions contained only sodium carbonate with the hypochlorite, the free alkali being converted into the carbonate by addition of the requisite amount of bicarbonate. Two series of experiments were made; in (a) a constant excess of sodium carbonate was used with varying amounts of hypochlorite, and in (b) a constant excess of hypochlorite with varying amounts of sodium carbonate. The results are given in Tables VI (a) and VI (b), and the values plotted in Figs. 1 and 2, respectively.

TABLE VI (a)

Na ₂ CO ₃ .	NaOCl.	Available oxygen.
1.240	0.280	0.560
1.230	0.512	0.705
1.238	1.045	0.730
1.238	1.546	0.768
1.230	2.043	0.782

TABLE VI (b).

Na ₂ CO ₃ .	NaOCl.	Available oxygen.
	1.011	0.495
	1.018	0.592
	1.011	0.671
	1.230	0.725
	1.541	0.792
	2.005	0.889
	2.511	1.011
	3.042	1.072

A ²

It is seen that the precipitated carbonate is oxidised by the hypochlorite. The available oxygen in the precipitate is about the same as in the case of the hydroxide, but calculated on the nickel taken it reaches a value only half as great; the liberated carbon dioxide combines with an equivalent amount of nickel carbonate, yielding the bicarbonate, so that only half the nickel is precipitated: $4\text{NiCO}_3 + 2\text{NaOCl} + 2\text{H}_2\text{O} = \text{Ni}_2\text{O}_3 + \text{O} + 2\text{Ni}(\text{HCO}_3)_2 + 2\text{NaCl}$. Increasing the excess of sodium carbonate by decreasing the extent of nickel bicarbonate formation produces an increase in the amount of nickel precipitated and consequently in the available oxygen calculated on the nickel taken.

Influence of Temperature.—In this series of experiments the composition of the reacting solutions was the same in each case. The solutions were brought to the requisite temperature before mixing and maintained at this temperature while stirred for an hour. They were allowed to settle over-night before being filtered and analysed.

(a) Precipitating solution, NaOH 1.80 equivs. NaOCl 1.95 equivs.

Temp. of precipitation	0°	15°	25°	40°	60°
Available oxygen	1.294	1.285	1.260	1.236	1.190

(b) Precipitating solution, $\text{Ca}(\text{OH})_2$ 1.90 equivs. $\text{Ca}(\text{OCl})_2$ 1.18 equivs.

Temp. of precipitation	0°	15°	30°	60°	75°	90°
Available oxygen	1.622	1.500	1.390	1.164	1.046	0.952

In both cases there is a decrease in the available oxygen with increase of temperature, and this is due to increase in the rate of decomposition of the precipitate. When plotted, the values fall on a straight line; decomposition proceeds smoothly beyond the sesquioxide stage. The loss of oxygen in (b) is much greater than in (a); the precipitate is stabilised by alkali, but the effect is small in the case of lime, since its active mass is limited by its sparing solubility.

Influence of Concentration.—In this series of experiments all conditions were constant except the concentration of the reacting solutions. In B the concentration was the same as in all the previous experiments; in A, it was half, and in C, double this value.

(a) Precipitating solution, NaOH 1.95 equivs. NaOCl 1.07 equivs.

	A	B	C
Concentration	half	unity	double
Available oxygen	1.224	1.237	1.272

(b) Precipitating solution, $\text{Ca}(\text{OH})_2$ 1.90 equivs. $\text{Ca}(\text{OCl})_2$ 1.10 equivs.

	A	B	C
Concentration	half	unity	double
Available oxygen	1.485	1.500	1.525

There is an increase in the oxygen content of the precipitate with increasing concentration, doubtless because of the increased protective effect of the alkali, which is much more marked with soda than with lime.

Summary.

1. Hypochlorites free from alkali react only slowly with nickel sulphate solution; the rate of the reaction is negligible compared with that in presence of alkali.
2. With excess of alkali, hypochlorites oxidise the precipitated nickel hydroxide. The action is quantitative beyond the sesquioxide stage, but, owing to catalytic decomposition by the peroxide formed, larger amounts of hypochlorite produce only a small proportionate increase in the oxygen content.
3. With sodium carbonate, hypochlorites similarly oxidise the precipitated nickel carbonate, but the liberated carbon dioxide yields nickel bicarbonate, so that precipitation is not complete.
4. The precipitate is very unstable and evolves oxygen even in suspension at the ordinary temperature. Decomposition proceeds beyond the sesquioxide stage; the rate is retarded by alkali.
5. A lower oxygen content results from precipitating at higher temperatures owing to the increased rate of decomposition of the precipitate.
6. There is an increase in the oxygen content with increasing concentration of the reacting solutions, probably owing to the increased protective effect of the alkali.

Differences in Behaviour of Cobalt and Nickel.

1. The peroxidised precipitate obtained with cobalt is stable; it can be kept for a long time or the suspension boiled without loss of oxygen. With nickel, the precipitate decomposes with evolution of oxygen even in suspension at the ordinary temperature and the oxygen content falls continuously below that corresponding to the sesquioxide; decomposition is accelerated by heat and retarded by alkali.
2. Hypochlorites free from alkali react immediately with cobalt solutions, yielding a peroxidised precipitate, the rate of the reaction being comparable with that of precipitation of the hydroxide by alkali and its oxidation by hypochlorite. With nickel, the action is delayed and is negligibly slow compared with the action in the presence of alkali.
3. In the presence of alkali, the hydroxides are peroxidised.

With cobalt, excess of hypochlorite causes a decrease in the oxygen content owing to its increased direct action; with nickel, it causes an increase owing to its further oxidising action. With cobalt, excess of alkali causes a small increase in the oxygen content owing to increased precipitation as hydroxide; with nickel, it causes a large increase owing to its retarding decomposition of the precipitate.

4. Precipitated with sodium carbonate and hypochlorite, cobalt salts yield a peroxidised carbonate; in the case of nickel, however, the precipitated carbonate is oxidised to the peroxide with loss of carbon dioxide, which yields the bicarbonate.

The author is indebted to Principal B. Mouat Jones and Professor T. C. James for giving him every facility for carrying out this work and to Professor T. M. Lowry for his kindly interest. He would also gratefully acknowledge the kindness of the Royal Commissioners for the Exhibition of 1851 in reserving the scholarship granted him in 1914 and resumed during this investigation.

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[Received, January 29th, 1923.]

LXXXI.—*Derivatives of Tetrahydrocarbazole. Part II.*

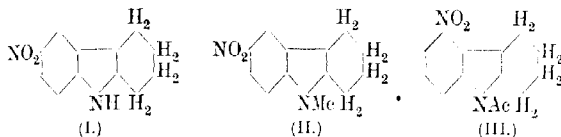
By WILLIAM HENRY PERKIN, jun., and SYDNEY GLENN PRESTON
PLANT.

IN the previous communication (T., 1921, **119**, 1825), we emphasised the importance attaching to tetrahydrocarbazole, not only on account of its close relationship to tetrahydroharnine, but also because there is reason to believe that strychnine and brucine are derivatives of this substance.

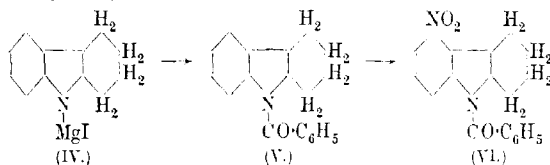
During the course of a long series of experiments on the synthesis of substances which it is thought may prove to be closely allied to strychnine, and the results of which it is hoped will shortly be ready for publication, it became increasingly important that the properties of tetrahydrocarbazole and its derivatives should be more completely studied.

The present communication contains a further description of experiments made with this object in view. Part I of this investigation (*loc. cit.*) was mainly concerned with the nitration of tetrahydrocarbazole, 9-methyltetrahydrocarbazole, and 9-acetyltetra-

hydrocarbazole* and it was pointed out that, whilst the parent substance and its 9-methyl derivative, when nitrated in strong sulphuric acid solution with potassium nitrate, give almost quantitative yields of the 6-nitro-derivatives (I and II), 9-acetyltetrahydrocarbazole, on treatment in acetic acid solution with nitric acid, is converted into the 5-nitro-derivative (III), a result quite unexpected and somewhat difficult to understand (compare p. 684).

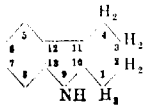


In connexion with our experiments on the action of nitric acid on 9-acetyltetrahydrocarbazole, it was clearly of interest to investigate the behaviour of 9-benzoyltetrahydrocarbazole under similar conditions, but this could not be done at the time because we were unable to prepare this benzoyl derivative from tetrahydrocarbazole by the action of benzoyl chloride. Subsequently we found that the following process works well, not only in the case of the benzoyl derivative, but also in the preparation of other 9-acyl derivatives of tetrahydrocarbazole. Tetrahydrocarbazole is added to an ethereal solution of magnesium ethyl iodide, when ethane is liberated and magnesium 9-tetrahydrocarbazyl iodide (IV) produced, and this reacts readily with benzoyl chloride, giving a good yield of 9-benzoyltetrahydrocarbazole (V):



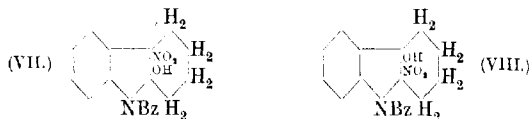
When the solution of 9-benzoyltetrahydrocarbazole in glacial acetic acid is mixed with nitric acid, it furnishes, as one of the products of the interaction, 5-nitro-9-benzoyltetrahydrocarbazole (VI; m. p. 140°), the constitution of which was proved by hydrolysis with alkali, when it yielded 5-nitrotetrahydrocarbazole with elimination of the benzoyl group.

* The scheme of numbering the positions in tetrahydrocarbazole used in this and in the previous communication is:

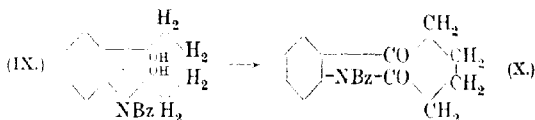


The main product of the action of nitric acid on 9-benzoyltetrahydrocarbazole is, however, a colourless, crystalline substance which melts at 150° with evolution of oxides of nitrogen. This substance has the formula $C_{19}H_{18}O_4N_2$, and therefore is produced from benzoyltetrahydrocarbazole, $C_{19}H_{17}ON$, by the addition of nitric acid and there can be no doubt that this addition takes place—in the form of $\cdot OH$ and $\cdot NO_2$ —at the double linking (10 and 11) of the partly reduced ring.

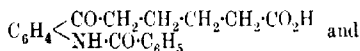
This addition may take place in two directions leading to the formulæ VII and VIII; of these we think VII the more probable



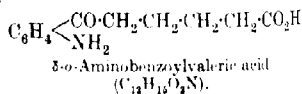
and therefore the substance $C_{19}H_{18}O_4N_2$ is named 11-nitro-9-benzoyl-10-hydroxyhexahydrocarbazole in this communication. The most remarkable decomposition of this substance is that brought about by boiling with potassium hydroxide, when it yields, as the main product, an acid, $C_{19}H_{19}O_4N$, melting at 124° , together with a small quantity of an acid, $C_{19}H_{17}O_3N$, which melts at 226° , the constitution of which is discussed below. The acid $C_{19}H_{19}O_4N$ is decomposed by boiling with excess of alkali into benzoic acid and an amino-acid, $C_{12}H_{15}O_3N$ (m.p. 129°); the former is therefore evidently the benzoyl derivative of the latter. The mechanism of this curious series of changes is probably the following: In the first place, the alkali converts 11-nitro-9-benzoyl-10-hydroxyhexahydrocarbazole into the corresponding 10:11-dihydroxy-derivative (IX); this then undergoes oxidation in the presence of the nitrite, and the intermediate substance (X) is produced.



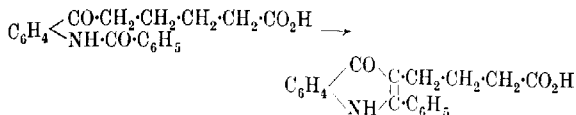
The substance (X) is then further acted on by the alkali, in two stages, yielding the acids



δ -o-Benzoylamino-benzoylvaleric acid ($C_{19}H_{19}O_4N$).



Neither of these acids appears to have been prepared, but the parent acid— δ -benzoylvaleric acid (m. p. 78°)—has been described and is produced by the condensation of benzene with the chloride of adipic acid (Bauer, *Compt. rend.*, 1912, **155**, 288; Borsche and Wollemann, *Ber.*, 1912, **45**, 3715). The acid $C_{19}H_{17}O_3N$ (m. p. 226°), produced in small quantity by the action of alkali on 11-nitro-9-benzoyl-11-hydroxyhexahydrocarbazole, is apparently produced from δ -*o*-benzoylaminobenzoylvaleric acid by internal condensation between the $>CO$ of the benzoyl group and the δ - $>CH_2$ of the valeric acid residue,



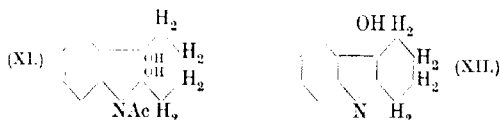
and is therefore probably γ -4-hydroxy-2-phenylquinoline-3-butyric acid.

Condensations of this kind do not appear to have been previously met with, but a somewhat similar change was observed by Perkin and Robinson (T., 1913, **103**, 1975), namely, the conversion of *o*-aldehydosuccinilic acid into carbostyryl-3-acetic acid by the action of alkali.

A preliminary investigation of the action of nitric acid on 9-acetyl-tetrahydrocarbazole was described in the previous communication (*loc. cit.*, p. 1828), and it was there shown that the main product, under the conditions employed at the time, is the 5-nitro-derivative (III).

In view, however, of the unusual course observed in the case of the interaction of the 9-benzoyl derivative and nitric acid, it seemed desirable to study more completely the action of nitric acid on the 9-acetyl derivative, and we now find that, if less acetic acid is used in this nitration than previously, there is produced, along with the 5-nitro-derivative, a new substance, $C_{14}H_{17}O_3N$, derived from 9-acetyltetrahydrocarbazole by the addition of two hydroxyl groups.

There can be little doubt that the addition again takes place at the unsaturated linking of the partly reduced ring and that the new substance is 9-acetyl-10 : 11-dihydroxyhexahydrocarbazole (XI).



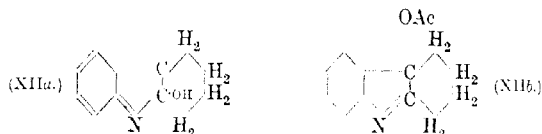
It is curious that the action of nitric acid on 9-benzoyl- and 9-acetyl-tetrahydrocarbazole should yield products of such different

kinds, for whereas, in the former case, the interaction results in the addition of nitric acid (p. 678), in the case now under discussion, the change depends on the addition of two hydroxyl groups.

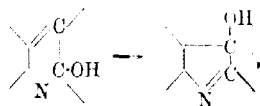
The investigation of (XI) has yielded very curious and unexpected results. In the first place, its behaviour towards alkalis was studied, when it was found that it dissolves in hot aqueous alcoholic potassium hydroxide to a deep red solution from which an orange substance melting at 79° separates. This substance has the formula $C_{12}H_{13}ON$, and therefore is obtained from XI ($C_{11}H_{17}O_3N$) by the removal of acetic acid. At first sight, the most probable explanation of this change is that it is brought about by the union of the 9-acetyl group with the neighbouring hydroxyl group, in which case the substance $C_{12}H_{13}ON$ will have the constitution represented by formula XII, and we suggest the name *11-hydroxy-tetrahydrocarbazolenine* for this substance. The presence of the hydroxyl group is confirmed by the fact that the substance yields a well-characterised, colourless acetyl derivative (m. p. 113°).

It is, however, by no means clear that the elimination of acetic acid during the formation of the substance $C_{12}H_{13}ON$ proceeds in the direct manner just suggested, for this view scarcely supplies the explanation of the fact that, whereas the acetyl derivative is colourless, the substance $C_{12}H_{13}ON$ is highly coloured. It is possible that the elimination of acetic acid may take place in such a way as to yield the isomeric hydroxy-derivative of the formula (XIIa). This formula would account for the inability of the substance to form an additive compound with methyl iodide and would also supply an explanation for its being coloured.

On the other hand, the colourless acetyl derivative probably has the constitution represented by formula (XIIb) derived from XII,



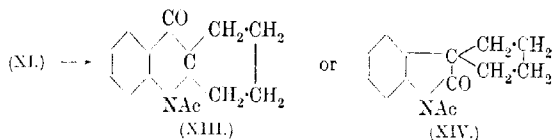
the tautomeric change incurred in the conversion of the substance into the acetyl derivative being that represented by the scheme



an interchange which would not be difficult to realise in the presence of dilute acids. Until, however, further evidence on this point has

been obtained we propose to retain the name 11-hydroxytetrahydrocarbazolenine for the substance $C_{12}H_{13}ON$.

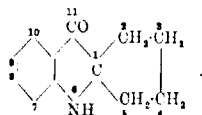
The most interesting property of 9-acetyl-10:11-dihydroxyhexahydrocarbazole is its behaviour on heating either alone or with acetic anhydride. Under these conditions, it yields a colourless, crystalline substance, $C_{14}H_{15}O_2N$ (m. p. 104°), produced from the acetyl derivative by the elimination of water; careful examination of this substance, however, clearly indicates that this is not a case of simple dehydration, but that some fundamental change in constitution has taken place, and the nature of this change proved for some time very puzzling. Ultimately Professor Robinson suggested that 9-acetyl-10:11-dihydroxyhexahydrocarbazole may be considered as a pinacol and that the elimination of water under the acidic conditions employed may give rise to pinacolin formation according to the scheme



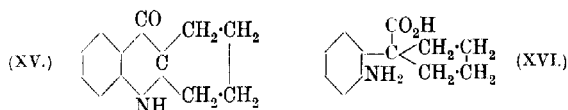
and of these alternatives (XIII) was considered the more probable on theoretical grounds.

The investigation of the properties of the substance $C_{14}H_{15}O_2N$ clearly suggests that this view of the mechanism of its formation is the correct one, but of the two formulæ, XIII and XIV, the latter seems to be out of the question for reasons stated below. Formula XIII represents the substance $C_{14}H_{15}O_2N$ as an acetyl derivative of a *spiro*-condensation product of *c*-indoxyl and cyclopentane and therefore we propose to name it 6-acetyl-*c*-indoxylspirocyclopentane.* On hydrolysis with excess of alcoholic potassium hydroxide, this substance loses the acetyl group and yields *c*-indoxylspirocyclopentane (XV), which crystallises in colourless plates, melts at 113° , and is reconverted into the acetyl derivative on treatment with acetic anhydride. This behaviour with excess of alkali seems to show that XIV cannot be the correct expression for the substance $C_{14}H_{15}O_2N$, because this structure represents the substance as an

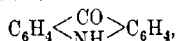
* The numbering of the positions in *c*-indoxylspirocyclopentane employed is:



acetyl-lactam, and this would yield the corresponding amino-acid (XVI) on hydrolysis, which, however, is not the case.

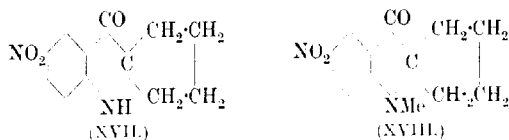


ψ -Indoxylspirocyclopentane is insoluble in dilute acids or alkalis and does not react with ethyl or methyl iodide or with methyl sulphate in the presence of potassium hydroxide. It also does not yield a nitroso-derivative or a semicarbazone. In these and other ways it exhibits properties similar to those of acridone,



which it resembles in constitution.

The properties of ψ -indoxylspirocyclopentane are, however, profoundly modified by nitration and the ease with which the nitro-derivative is produced is remarkable, the conversion being rapid and complete when the substance is boiled for a few minutes with 20 per cent. nitric acid. The nitro-derivative crystallises in brown prisms, melts at 229° , and is presumably 9-nitro- ψ -indoxylspirocyclopentane (XVII).



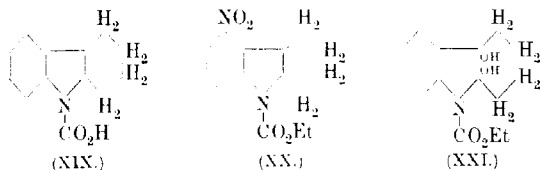
Unlike the parent substance, this nitro-derivative dissolves readily in dilute sodium hydroxide, giving a deep yellow solution, and is reprecipitated on the addition of hydrochloric acid. When the solution in sodium hydroxide is treated with methyl sulphate, a colourless monomethyl derivative (XVIII; m. p. 142°) is formed in which the methyl group is attached to nitrogen, because it is not removed by boiling with hydriodic acid.

In view of the remarkable differences in behaviour exhibited by 9-benzoyl- and 9-acetyl-tetrahydrocarbazole on treatment with nitric acid, it seemed of interest to investigate the action of nitric acid on other *N*-acyl derivatives of somewhat different character, and therefore we prepared *ethyl t-tetrahydrocarbazole-9-carboxylate* and studied its behaviour with nitric acid. Tetrahydrocarbazole-9-carboxylic acid (XIX) may be obtained by passing carbon dioxide into the ethereal solution of magnesium 9-tetrahydrocarbazyl

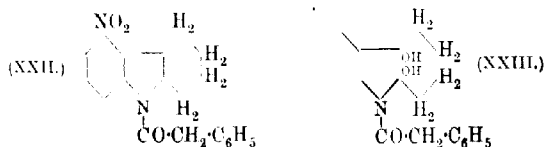
iodide (IV), but it is an unstable substance which slowly loses carbon dioxide, with regeneration of tetrahydrocarbazole, at the ordinary temperature and very readily on warming. The sodium salt also rapidly decomposes, but the ethyl ester is quite stable and may be readily obtained in a state of purity. The *ethyl tetrahydrocarbazole-9-carboxylate* used in our experiments was prepared from magnesium 9-tetrahydrocarbazyl iodide by the action of ethyl chloroformate; it separates from alcohol in colourless needles and melts at 65°.

When it is treated with nitric acid in glacial acetic acid solution, oxides of nitrogen are evolved and two substances produced, one of which is *ethyl 5-nitrotetrahydrocarbazole-9-carboxylate* (XX; m. p. 116°) because, on boiling with potassium hydroxide, it yields 5-nitrotetrahydrocarbazole.

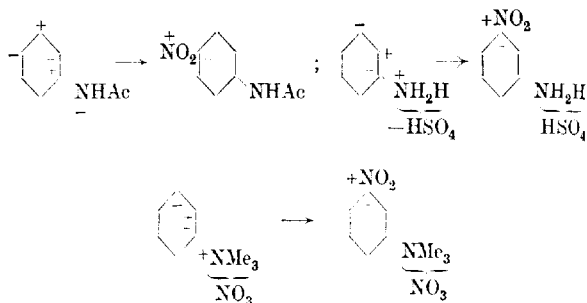
The second substance, $C_{15}H_{19}O_4N$, crystallises in colourless needles (m. p. 133°) and is evidently *ethyl 10:11-dihydroxyphenyltetrahydrocarbazole-9-carboxylate* (XXI), produced by the addition of two hydroxyl groups to the 10:11-position exactly as happened in the case of the action of nitric acid on 9-acetyltetrahydrocarbazole. In proof of this, we find that, on hydrolysis with potassium hydroxide, the substance XXI yields 11-hydroxytetrahydrocarbazolenine (XII).



The action of nitric acid in glacial acetic acid on 9-phenylacetyl-tetrahydrocarbazole, a crystalline substance, m. p. 86°, readily obtained by the action of phenylacetyl chloride on the ethereal solution of magnesium 9-tetrahydrocarbazyl iodide, follows the same course as in the corresponding cases of 9-acetyltetrahydrocarbazole and ethyl tetrahydrocarbazole-9-carboxylate. The product consists of 5-nitro-9-phenylacetyltetrahydrocarbazole (XXII) and a substance, $C_{20}H_{21}O_3N$, which melts at 169° and is evidently 9-phenylacetyl-10:11-dihydroxyphenyltetrahydrocarbazole (XXIII).

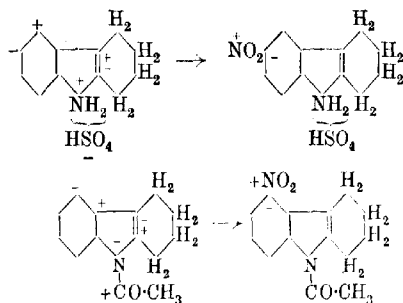


It has already been pointed out (T., 1921, 119, 1828) that the study of the nitration of tetrahydrocarbazole and its *N*-substitution derivatives has brought to light examples of apparent reversal of the ordinary rules of substitution. When tetrahydrocarbazole or its 9-methyl derivative is nitrated in sulphuric acid solution, the nitro-group enters the 6- or para-position to the $>\text{NH}$ or $>\text{NMe}$ group, yielding in the case of tetrahydrocarbazole the 6-nitro-derivative (I). On the other hand, each of the *N*-acyl derivatives investigated has yielded, on nitration in acetic acid solution, derivatives in which the nitro-group has taken up the position 5, which may be considered as meta to the $>\text{NH}$ group. For example, 9-acetyltetrahydrocarbazole yields on nitration 5-nitro-9-acetyl-tetrahydrocarbazole (III). These results are directly contrary to the usual experience, as is evident from the consideration of the following scheme :



In view of this discrepancy, we have discussed the matter with Professor Robinson and he has kindly suggested the following explanation.

The experiments recorded in the present communication on the addition of nitric acid to the double linking in derivatives of tetrahydrocarbazole clearly show that the ethylene linking in tetrahydrocarbazole is a very active one and the orienting influence is evidently transmitted through it. The nitrogen atom is responsible for this activation of the bond, and the effect of the nitrogen atom on the aromatic nucleus must pass through this bond. This view clears up the whole difficulty because, in passing through the ethylene linking, position 5 becomes the para- and 6 the meta-position. The schemes of nitration of tetrahydrocarbazole, in sulphuric acid solution, and of 9-acetyltetrahydrocarbazole then become :



In addition to the experiments on the action of nitric acid on the acyl derivatives of tetrahydrocarbazole recorded above, we have also made further attempts to find a satisfactory method for the conversion of derivatives of tetrahydrocarbazole into the corresponding derivatives of carbazole. In Part I of this investigation (*loc. cit.*, p. 1830) we converted tetrahydrocarbazole into carbazole, and 9-methyltetrahydrocarbazole into 9-methylcarbazole, by boiling with mercuric acetate in acetic acid solution, but the yields were most unsatisfactory. We now find that better results are obtained when the solution of the tetrahydro-derivative in quinoline is boiled with the calculated amount of sulphur; this process is successful, not only in the cases just mentioned, the yields varying from 15–30 per cent. of those theoretically possible, but also in the conversion of 9-acetyltetrahydrocarbazole and 6-bromotetrahydrocarbazole into the corresponding carbazole derivatives.

EXPERIMENTAL.

Action of Nitric Acid on 9-Benzoyltetrahydrocarbazole (V). Formation of 11-nitro-9-benzoyl-10-hydroxyhexahydrocarbazole (VII).

The solution of magnesium ethyl iodide obtained from ethyl iodide (32 grams), magnesium turnings (4.8 grams), and dry ether (450 c.c.) is gradually mixed with tetrahydrocarbazole (34 grams); interaction proceeds steadily with evolution of ethane and is completed by warming for a few minutes on the steam-bath. Addition of freshly distilled benzoyl chloride (28.5 grams) causes considerable evolution of heat, a heavy viscous layer separates and, after standing, the whole is warmed for a few minutes and decomposed by ice and water. The ethereal solution of the crude 9-benzoyltetrahydrocarbazole is washed with dilute hydrochloric acid, dried over calcium chloride, filtered from a sticky brown substance, and the ether removed. A syrupy mass remains which cannot be made to

crystallise until it is distilled, when most of it passes over at 235–265°/13 mm. as a pale yellow oil which, in contact with alcohol, soon crystallises and then separates from alcohol in colourless plates melting at 85° (Found: N = 5.0. $C_{19}H_{17}ON$ requires N = 5.1 per cent.). On boiling with aqueous alcoholic potassium hydroxide, this benzoyl derivative is readily hydrolysed and, on adding water, tetrahydrocarbazole separates.

Action of Nitric Acid.—In this experiment, the solution of 9-benzoyltetrahydrocarbazole (14 grams) in glacial acetic acid (180 c.c.) was warmed at 30°, vigorously stirred, and nitric acid (5.1 grams of *d* 1.4) gradually added. In a few minutes a colourless, crystalline solid separated which, after remaining for four hours, was collected and washed with acetic acid. This substance (6.3 grams)—11-nitro-9-benzoyl-10-hydroxyhexahydrocarbazole (VII)—melts at 150° with evolution of oxides of nitrogen, and a similar decomposition takes place when it is boiled with glacial acetic acid (Found: C = 67.5; H = 5.3; N = 8.3. $C_{19}H_{15}O_4N_2$ requires C = 67.5; H = 5.3; N = 8.3 per cent.).

The action of potassium hydroxide on this substance is described in the next section.

The acetic acid filtrate from the above substance yielded, on dilution with water, a yellow mass which, after two crystallisations from methyl alcohol, was obtained in bright yellow prisms melting at 140° and proved to be 5-nitro-9-benzoyltetrahydrocarbazole (VI) (Found: N = 8.5. $C_{19}H_{15}O_3N_2$ requires N = 8.7 per cent.).

This benzoyl derivative was hydrolysed by boiling for half an hour with aqueous alcoholic potassium hydroxide and, on adding water, a yellow solid separated, m. p. 171°; after recrystallisation, it was shown, by the melting point of the mixture, to be identical with 5-nitrotetrahydrocarbazole (m. p. 172°) which had previously been obtained from 5-nitro-9-acetyltetrahydrocarbazole by hydrolysis (T., 1921, 119, 1836).

Action of Potassium Hydroxide on 11-Nitro-9-benzoyl-10-hydroxyhexahydrocarbazole (VII). Formation of δ -o-Benzoylaminobenzoylvaleric Acid, δ -o-Aminobenzoylvaleric Acid, and γ -4-Hydroxy-2-phenylquinoline-3-butyric Acid (p. 678).

In studying this decomposition, the 9-benzoyl derivative (13 grams) was boiled for fifteen minutes with potassium hydroxide (26 grams) dissolved in water (180 c.c.) and alcohol (300 c.c.), and, after cooling and diluting with water, the clear solution was acidified with hydrochloric acid.

Occasionally δ -o-benzoylaminobenzoylvaleric acid separates as a colourless solid, but more frequently as an oil which solidifies on

standing and rubbing; it then melts at 124° and, after crystallisation from alcohol, from which it separates in colourless needles (7 grams), at 126° (Found: C = 70.2; H = 5.9; N = 4.2. $C_{19}H_{19}O_4N$ requires C = 70.2; H = 5.8; N = 4.3 per cent.). The sodium salt is obtained in silky needles on rubbing the acid with sodium carbonate or hydroxide solution; it dissolves in warm water and separates again on cooling.

When the acid (6 grams) is heated on the steam-bath for an hour with excess of potassium hydroxide (17 grams), dissolved in water (110 c.c.), a clear solution results from which, on cooling and acidifying with hydrochloric acid, crude γ -4-hydroxy-2-phenylquinoline-3-butyric acid, which is described below, separates. The filtrate from this acid contains δ -o-aminobenzoylvaleric acid, which is isolated by making the solution just alkaline with potassium hydroxide and then acidifying with acetic acid. The acid (3.5 grams) is precipitated as a pale yellow solid which melts at 129° , and this melting point is not altered by recrystallisation from dilute alcohol, from which the acid separates in yellow prisms (Found: C = 65.2; H = 6.8. $C_{12}H_{15}O_3N$ requires C = 65.2; H = 6.8 per cent.).

This acid dissolves in hydrochloric acid (1 vol. of concentrated acid + 1 vol. of water), but almost immediately a crystalline mass of the hydrochloride separates.

The addition of sodium nitrite produces a clear solution of the diazonium chloride, which couples with alkaline β -naphthol to give a red dye, and this behaviour confirms the presence of an amino-group.

Attempts to prepare an oxime, phenylhydrazone, and semicarbazone of the amino-acid were unsuccessful.

γ -4-Hydroxy-2-phenylquinoline-3-butyric Acid:—The crude acid, obtained as described above, contains varying quantities of δ -o-aminobenzoylvaleric acid. On boiling with toluene, this dissolves and, after filtering, is deposited from the filtrate in crystals, whereas the quinoline derivative remains and may be purified by recrystallisation from dilute alcohol. The colourless needles which separate contain water of crystallisation (Found: C = 69.8; H = 6.1; N = 4.5. $C_{19}H_{17}O_3N \cdot H_2O$ requires C = 70.2; H = 5.8; N = 4.3 per cent.). On heating in a capillary tube, the loss of water is rapid at 160° and the residue melts sharply at 226° (Found: C = 74.0; H = 5.9; N = 5.0. $C_{19}H_{17}O_3N$ requires C = 74.3; H = 5.5; N = 4.6 per cent.). The yield of this acid which is produced from 11-nitro-9-benzoyl-10-hydroxyhexahydrocarbazole under the conditions described above was small and did not amount to more than 0.35 gram from 6 grams.

Action of Nitric Acid on 9-Acetyltetrahydrocarbazole. Formation of 9-Acetyl-10:11-dihydroxyhexahydrocarbazole (XI) and 11-Hydroxytetrahydrocarbazolenine (XII).

The conversion of 9-acetyltetrahydrocarbazole into the 5-nitro-derivative by the addition of nitric acid to the solution in much acetic acid has been described in the previous communication (T., 1921, 119, 1836). We have now ascertained that the interaction proceeds in an entirely different direction in the presence of a much smaller quantity of acetic acid and under the following conditions. The acetyl derivative (16.5 grams), dissolved in glacial acetic acid (45 c.c.) at 30°, is mixed with nitric acid (7.8 grams of *d* 1.4), diluted with acetic acid (12 c.c.). The temperature rises to 60°, considerable quantities of oxides of nitrogen are liberated, and in a short time crystallisation commences. After several hours, the solid is collected and washed with a little acetic acid; it now weighs 12.6 grams, melts indefinitely at 155–190°, and is evidently a mixture. If this mixture is dissolved in boiling alcohol (800 c.c.) and the filtered solution allowed to remain undisturbed, 5-nitro-9-acetyltetrahydrocarbazole alone separates in long needles melting at 174°. The filtrate from this substance deposits, on stirring and long standing, small, colourless, glistening plates which melt at 204°; the melting point is not altered by recrystallisation from alcohol.

The mother-liquors yield, on concentrating, a crop of crystals which again are a mixture of the nitro-derivative and the substance melting at 204°. The original product of the action of nitric acid appears to consist roughly of 20 per cent. of the former and 80 per cent. of the latter, which is 9-acetyl-10:11-dihydroxyhexahydrocarbazole (Found: C = 68.0; H = 6.9; N = 5.4. $C_{14}H_{17}O_2N$ requires C = 68.0; H = 6.9; N = 5.7 per cent.). This substance is very soluble in warm alcohol and in boiling acetic acid and separates from the latter, on cooling, in well-developed, flat prisms, which are sparingly soluble in benzene or light petroleum, and more readily soluble in chloroform. It is coloured red by sulphuric acid and dissolves to a deep yellow solution; no immediate change is produced by the addition of a drop of nitric acid, but on standing the colour changes to deep brown.

Action of Potassium Hydroxide.—9-Acetyl-10:11-dihydroxyhexahydrocarbazole dissolves to a red solution when it (1.3 grams) is heated to boiling for half an hour with potassium hydroxide (3.2 grams), dissolved in water (10 c.c.) and alcohol (15 c.c.); on adding water to the cold product, an oil separates which soon solidifies to a red mass. This substance, which is obtained in

almost quantitative yield, separates from light petroleum in long, orange prisms and melts at 79° (Found: C = 77.1; H = 6.9. $C_{12}H_{13}ON$ requires C = 77.0; H = 6.9 per cent.). This analysis shows that the action of alkali on 9-acetyl-10:11-dihydroxyhexahydrocarbazole had brought about the elimination of acetic acid.

The substance $C_{12}H_{13}ON$ has been named 11-hydroxytetrahydrocarbazolenine, and its constitution is discussed on p. 680. It is soluble in hot water, yielding a nearly colourless solution possessing a pale blue fluorescence; the solution in methyl alcohol also has a striking fluorescence, but this is destroyed by the addition of a drop of ferric chloride without the production of any coloration. It is very soluble in benzene, but sparingly soluble in light petroleum, and separates from a mixture of these solvents in needles which have a red shade. The crystals on crushing yield a bright yellow powder. When heated in small quantities, the substance distils unchanged and without any residue, and the distillate solidifies to an orange-red, crystalline mass melting at $78-79^{\circ}$.

The substance $C_{12}H_{13}ON$ could not be made to combine with either methyl or ethyl iodide, but an acetyl derivative was obtained by boiling it with acetic anhydride for four hours. The product, on the addition of water, deposited an oil which soon solidified, and the acetyl derivative separated from light petroleum in colourless prisms (Found: C = 73.4; H = 6.5. $C_{14}H_{15}O_2N$ requires C = 73.4; H = 6.5 per cent.).

11-Acetoxytetrahydrocarbazolenine melts at 113° and is isomeric with acetyl- ψ -indoxylspirocyclopentane (m. p. 104° ; see the next section). It is hydrolysed to 11-hydroxytetrahydrocarbazolenine when it is warmed with methyl alcoholic potassium hydroxide.

ψ -Indoxylspirocyclopentane (XV).

Acetyl- ψ -indoxylspirocyclopentane (XIII) is obtained when 9-acetyl-10:11-dihydroxyhexahydrocarbazole (XI) is either digested with acetic anhydride or simply strongly heated. (1) The 9-acetyl derivative (2.5 grams) was boiled with acetic anhydride (40 c.c.) for two hours and the clear solution, from which nothing separated on cooling, mixed with water and well shaken. The yellow solid which separated crystallised from alcohol in long, colourless prisms and melted at 104° (Found: C = 73.7; H = 6.5. $C_{14}H_{15}O_2N$ requires C = 73.4; H = 6.5 per cent.).

(2) The 9-acetyl derivative (0.5 gram) was heated in a sulphuric acid bath at 225° for about thirty seconds, when it effervesced and water and some acetic acid distilled and condensed on the cold part of the test-tube. The residual brown syrup set to a resin, which

solidified when rubbed with methyl alcohol, and the substance then separated from methyl alcohol in colourless prisms melting at 104° (Found: C = 73.3; H = 6.5; N = 6.1. $C_{14}H_{15}O_2N$ requires C = 73.4; H = 6.5; N = 6.1 per cent.).

That the substances produced by the different methods I and II are identical was proved by the method of mixed melting points.

Acetyl-ψ-indoxylspirocyclopentane is readily soluble in hot methyl alcohol, but much less so in the cold, and separates in long, colourless, flat needles. It is very readily soluble in benzene, but sparingly soluble in light petroleum, and crystallises from the mixture in well-developed, flat prisms. The solution in concentrated sulphuric acid is colourless and no colour develops on the addition of a drop of nitric acid. The acetyl derivative distils at a high temperature without decomposition, since the distillate melts directly at $98-102^{\circ}$ and, after recrystallisation, at 104° . The hydrolysis of this acetyl derivative may be brought about by boiling the substance (1 gram) for half an hour with potassium hydroxide (3 grams), dissolved in water (10 c.c.) and alcohol (15 c.c.). The solution, on cooling and diluting with water, deposited an oil which soon solidified to a colourless mass melting at 112° and, after recrystallisation from light petroleum, from which it separated in colourless plates, at 113° (Found: C = 77.0; H = 7.1. $C_{12}H_{13}ON$ requires C = 77.0; H = 6.9 per cent.). Another method which may be used for the hydrolysis of acetyl-ψ-indoxylspirocyclopentane is treatment with magnesium methyl iodide. The acetyl derivative (2 grams) was added to an ethereal solution of magnesium methyl iodide, prepared from magnesium turnings (0.85 gram) and methyl iodide (5 grams), and, after boiling for half an hour, the whole was decomposed by dilute hydrochloric acid. The ethereal solution, dried over sodium sulphate and evaporated, deposited an oil which soon solidified and, on crystallisation from alcohol, colourless plates of pure ψ-indoxylspirocyclopentane were obtained melting at 113° .

Experiment showed that magnesium methyl iodide may be employed in a similar manner for converting 9-acetyltetrahydrocarbazole into tetrahydrocarbazole.

ψ-Indoxylspirocyclopentane is not dissolved by boiling dilute acids or alkalis and does not yield a nitroso-derivative when sodium nitrite is added to the alcoholic solution containing hydrochloric acid. It is not acted on by methyl or ethyl iodide or when methyl sulphate is added to its solution in dilute methyl alcoholic potassium hydroxide. It does not react when its alcoholic solution is boiled with concentrated aqueous semicarbazide acetate. Boiling with acetic anhydride converts it into acetyl-ψ-indoxylspirocyclopentane (m. p. 104° . See above.).

Action of Dilute Nitric Acid on ψ -Indoxylspirocyclopentane. Formation of 9-Nitro- ψ -indoxylspirocyclopentane (XVII).

One of the most remarkable properties of ψ -indoxylspirocyclopentane is the ease with which it is nitrated even by quite dilute nitric acid, the yield of nitro-derivative being almost quantitative. The substance (1.2 grams) was added to a mixture of nitric acid (10 c.c. of *d* 1.4) and water (40 c.c.), and the whole gradually heated and finally boiled for three minutes with constant shaking. The green oil first formed soon solidified to a yellow, crystalline mass, and this was collected, well washed, and crystallised from alcohol, from which it separated in yellow-brown prisms melting at 229° (Found: C = 62.7; H = 5.4; N = 12.0. $C_{12}H_{12}O_3N_2$ requires C = 62.1; H = 5.2; N = 12.0 per cent.).

9-Nitro- ψ -indoxylspirocyclopentane, like ψ -indoxylspirocyclopentane, is insoluble in boiling dilute aqueous sodium carbonate, but it differs from the parent substance in being readily dissolved to a deep yellow solution by warm dilute sodium hydroxide. If the solution is concentrated, the yellow sodium derivative separates, which is readily soluble in water; addition of hydrochloric acid discharges the colour and the 9-nitro-derivative separates.

9-Nitro-6-methyl- ψ -indoxylspirocyclopentane (XVIII).—This characteristic derivative is obtained when 9-nitro- ψ -indoxylspirocyclopentane, dissolved in excess of warm dilute sodium hydroxide, is vigorously shaken with an excess of methyl sulphate. After heating for twenty minutes on the steam-bath, the methyl derivative is collected and recrystallised from alcohol, from which it separates in colourless plates melting at 142° (Found: C = 63.3; H = 5.7. $C_{13}H_{14}O_3N_2$ requires C = 63.4; H = 5.7 per cent.).

When the substance was heated with hydriodic acid, under the usual conditions of the Zeisel experiment, no methyl iodide was obtained; it is therefore evident that the methyl group is attached to nitrogen and is not present as methoxyl.

Tetrahydrocarbazole-9-carboxylic Acid (XIX).

This very unstable acid is obtained when carbon dioxide reacts with the magnesium iodide derivative of tetrahydrocarbazole. Magnesium ethyl iodide, prepared from magnesium (1.6 grams), ethyl iodide (10.6 grams), and dry ether (50 c.c.), was gradually mixed with tetrahydrocarbazole (11.3 grams); when interaction was complete, a slow stream of dry carbon dioxide was passed, a sticky brown substance separating. On adding hydrochloric acid (12 c.c.), diluted with an equal volume of water, the acid separated as a colourless solid, which was collected, washed with dilute hydro-

chloric acid, and left to dry on porous porcelain. The *tetrahydrocarbazole-9-carboxylic acid* obtained in this way is, however, never quite free from tetrahydrocarbazole, because the free acid gradually decomposes on keeping with loss of carbon dioxide, a decomposition which is much accelerated by warming. The solution of the acid in sodium hydroxide also gradually decomposes with separation of tetrahydrocarbazole.

The *Ethyl Ester*.—This derivative, unlike the free acid, is quite stable and may be conveniently prepared in the following manner.

Tetrahydrocarbazole (5.8 grams) is gradually added to magnesium ethyl iodide, prepared from magnesium (0.8 gram), ethyl iodide (5.3 grams), and dry ether (100 c.c.), and the whole is warmed for a few minutes to complete the reaction. Ethyl chloroformate (3.7 grams), dissolved in a little dry ether, is then run in slowly, when interaction takes place readily with evolution of heat and a colourless solid separates. After remaining for an hour, the whole is decomposed by dilute hydrochloric acid, the ethereal solution well washed, dried over calcium chloride, and the solvent removed by evaporation. The oil which remains crystallises in contact with alcohol and separates from this solvent in colourless, silky needles melting at 65° (Found: N = 5.9. $C_{13}H_{17}O_2N$ requires N = 5.8 per cent.).

When *ethyl tetrahydrocarbazole-9-carboxylate* is boiled with alcoholic potassium hydroxide, it is readily hydrolysed, and, on adding water, tetrahydrocarbazole separates. Attempts to convert the ethyl ester into the corresponding amide by heating with ammonia were unsuccessful.

Action of Nitric Acid on Ethyl Tetrahydrocarbazole-9-carboxylate.

As in the case of 9-acetyltetrahydrocarbazole, the action of nitric acid on this ester gives rise almost exclusively to two products, namely, ethyl 5-nitrotetrahydrocarbazole-9-carboxylate (XX) and ethyl 10:11-dihydroxytetrahydrocarbazole-9-carboxylate (XXI). The separation of these substances may be comparatively easily accomplished if the following conditions are observed. The ester (12.2 grams), dissolved in glacial acetic acid (20 c.c.) at the ordinary temperature, is gradually mixed with nitric acid (5 grams of *d* 1.4) diluted with acetic acid (5 c.c.), the whole being well stirred and care being taken that the temperature does not rise above 50°. During the action, oxides of nitrogen are liberated in quantity, and a clear solution results from which yellow needles of *ethyl 5-nitrotetrahydrocarbazole-9-carboxylate* soon begin to separate.

After standing for some time (usually about an hour), colourless crystals begin to appear. The whole is then immediately filtered

and the residue recrystallised from alcohol, from which the nitro-ester separates in long, yellow needles melting at 116° (Found: $N = 9.9$. $C_{15}H_{16}O_4N_2$ requires $N = 9.7$ per cent.).

When ethyl 5-nitrotetrahydrocarbazole-9-carboxylate is boiled for a few minutes with aqueous alcoholic potassium hydroxide, a deep red solution is obtained, from which 5-nitrotetrahydrocarbazole (m. p. 172°) is precipitated on the addition of water.

The acetic acid mother-liquors of the 5-nitro-ester deposit, on long standing, a mixture of ethyl 10:11-dihydroxyhexahydrocarbazole-9-carboxylate with small quantities of the 5-nitro-ester, and these substances may be separated by fractional crystallisation from alcohol, the 5-nitro-ester crystallising first. By repeating the process, *ethyl 10:11-dihydroxyhexahydrocarbazole-9-carboxylate* is obtained pure in colourless needles melting at $132-133^{\circ}$ (Found: $C = 65.1$; $H = 6.7$; $N = 4.8$. $C_{15}H_{19}O_4N$ requires $C = 65.0$; $H = 6.9$; $N = 5.0$ per cent.).

On boiling this ester with a solution of potassium hydroxide in aqueous alcohol, a deep red solution results, from which a red solid separates on the addition of water. This substance separated from light petroleum in orange prisms, melted at 79° , and was shown by a mixed melting point determination to be 11-hydroxytetrahydrocarbazoline (XII).

9-Phenylacetyltetrahydrocarbazole.

This substance may be obtained by a method similar to that employed in the preparation of the corresponding benzoyl derivative (p. 685).

Tetrahydrocarbazole (17 grams) is added to the Grignard compound prepared from magnesium (2.4 grams), ethyl iodide (15.6 grams), and dry ether (100 c.c.), and then phenylacetyl chloride (15.5 grams), dissolved in a little ether, gradually run in with continuous stirring. After warming for a few minutes, the mixture, from which a sticky oil will have separated, is decomposed by dilute hydrochloric acid, the ethereal solution washed, dried over calcium chloride, and the ether removed, when crude 9-phenylacetyltetrahydrocarbazole remains as an oil which gradually becomes partly solid. As this crude product could not be purified by crystallisation, it was distilled and the fraction $270-280^{\circ}/13$ mm. stirred with alcohol, when it crystallised and the substance then separated from alcohol in long needles melting at 86° . The yield did not amount to more than 35 per cent. of that theoretically possible (Found: $N = 4.7$. $C_{20}H_{19}ON$ requires $N = 4.8$ per cent.).

Action of Nitric Acid.—On treatment with nitric acid, 9-phenylacetyltetrahydrocarbazole behaves similarly to the corresponding

acetyl derivative (p. 688). The phenylacetyl derivative (7.5 grams), dissolved in glacial acetic acid (20 c.c.) at 60°, was gradually mixed with nitric acid (2.7 grams of *d* 1.4), when the temperature rose to 80°, oxides of nitrogen escaped, and almost immediately yellow needles began to form. After five hours, the precipitate was collected and recrystallised from much alcohol, from which 5-nitro-9-phenylacetyl-tetrahydrocarbazole separated in yellow needles melting at 178° (Found : N = 8.4. $C_{20}H_{18}O_3N_2$ requires N = 8.4 per cent.).

The constitution of this substance was proved by hydrolysis with aqueous alcoholic potassium hydroxide in the usual manner, when it yielded 5-nitrotetrahydrocarbazole.

The acetic acid mother-liquors of the 5-nitro-9-phenylacetyl derivative gradually deposited small, colourless, glistening prisms; after remaining over-night, these were collected and recrystallised from alcohol, from which the new substance separated in colourless prisms melting at 169° (Found : C = 74.1; H = 6.6. $C_{20}H_{21}O_3N$ requires C = 74.3; H = 6.5 per cent.). This substance is clearly 9-phenylacetyl-10 : 11-dihydroxyhexahydrocarbazole (XXIII), as the following behaviour proves. The substance (0.9 gram) was heated with acetic anhydride (17 c.c.) to boiling for four hours, and the clear solution mixed with water, when an oil was deposited which, in contact with light petroleum, soon crystallised. On recrystallisation from alcohol, colourless plates separated which melted at 78°.

That this substance is 6-phenylacetyl- ψ -indorylspirocyclopentane was shown by hydrolysis with aqueous alcoholic potassium hydroxide, when it yielded crystals melting at 113° which were proved by a mixed melting point determination to be ψ -indorylspirocyclopentane (XV).

Action of Sulphur on Tetrahydrocarbazole and its Derivatives.

Owing to the fact that carbazole and its derivatives react with sulphur with evolution of hydrogen sulphide, it is necessary to employ only sufficient sulphur to remove the added hydrogen. The best results were obtained when the reactions were carried out in the presence of some high-boiling solvent such as naphthalene or quinoline.

Conversion of Tetrahydrocarbazole into Carbazole.—Tetrahydrocarbazole (6 grams) and sulphur (2.25 grams) were heated with quinoline (20 c.c.) to boiling for thirty minutes, during which hydrogen sulphide escaped. The product was poured into a mixture of ice and excess of dilute hydrochloric acid, and the yellow-brown precipitate collected, washed with water, dried, and extracted with boiling toluene. On cooling, a mass of almost colourless crystals

(1.8 grams) separated, which melted at 230° and consisted of carbazole. In this and other similar experiments, pure quinoline must be used, because if crude coal tar quinoline is employed, a resinous product results from which very little crystalline substance can be extracted by toluene.

In testing the general applicability of this process the following experiments were made.

9-Methyltetrahydrocarbazole (3 grams), sulphur (1.05 grams), and quinoline (10 c.c.) were heated together for twenty-five minutes. On pouring the product into dilute hydrochloric acid, an oil separated, which soon solidified. The substance, which melted at $83-84^{\circ}$ after crystallisation from alcohol, consisted of 9-methylcarbazole (m. p. 86°), as a mixed melting point showed. The yield was, however, only 15 per cent.

9-Acetyltetrahydrocarbazole (5 grams) was then heated with sulphur (1.5 grams) and quinoline (15 c.c.) to boiling for half an hour. On treatment with dilute hydrochloric acid, an oil resulted which soon solidified to a brown mass, and this separated from light petroleum in needles melting at about 69° . That this substance was nearly pure 9-acetylcarbazole (m. p. 75°) was shown by a mixed melting point determination. The yield was about 22 per cent.

6-Bromotetrahydrocarbazole (3.2 grams) was boiled with quinoline (10 c.c.) and sulphur (0.82 gram) for twenty-five minutes, and the product poured into dilute hydrochloric acid, when a yellow solid was obtained which, after crystallisation from toluene, melted at about 186° , the yield being 20 per cent. of theory. That this substance was nearly pure 3-bromocarbazole (m. p. 197°) was shown by a mixed melting point determination, carried out with a specimen of this substance which had been obtained by brominating 9-acetylcarbazole and then removing the acetyl group.

Borsche, Witte, and Bothe (*Annalen*, 1908, 359, 58) found that tetrahydrocarbazole and certain of its derivatives can be oxidised to carbazole, etc., by distilling over lead oxide, but their method fails in the case of halogen- or nitro-derivatives. We have also found that the sulphur process is not applicable to 6-nitrotetrahydrocarbazole, the product being black and resinous. An experiment was also made on the action of sulphur (1.6 grams) on the boiling solution of ethyl tetrahydrocarbazole-9-carboxylate (6 grams) in quinoline (15 c.c.), but the product, on extraction with toluene, yielded only carbazole (1.4 grams).

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[Received, January 22nd, 1923.]

LXXXII.—*The Conditions of Reaction of Hydrogen with Sulphur. Part I. Direct Union.*

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RIDEAL.

THE interaction of hydrogen and sulphur at temperatures below the boiling point of the latter has been investigated by Hautefeuille (*Compt. rend.*, 1867, **64**, 610), Pelabon (*ibid.*, 1897, **124**, 686), and Bodenstein (*Z. physikal. Chem.*, 1899, **29**, 315). The work of the latter two investigators was, however, in disagreement, and after a somewhat lengthy controversy (Duhem, *ibid.*, p. 711; Bodenstein, *ibid.*, 1899, **30**, 567) the whole subject was apparently dropped and left in an unsatisfactory condition.

Pelabon (*loc. cit.*) states that combination between hydrogen and sulphur occurs down to a limiting temperature of 215° . Between the latter temperature and 350° combination is limited, but not by the reverse reaction, since hydrogen sulphide is not appreciably dissociated at these temperatures. In other words, according to this investigator the state of equilibrium obtained is different according as hydrogen sulphide or a mixture of hydrogen and sulphur is heated. Above 350° , the same equilibrium is attained from both sides. Pelabon cited these facts as evidence for including the formation of hydrogen sulphide from its elements in the class of reactions showing false or suspended equilibrium.

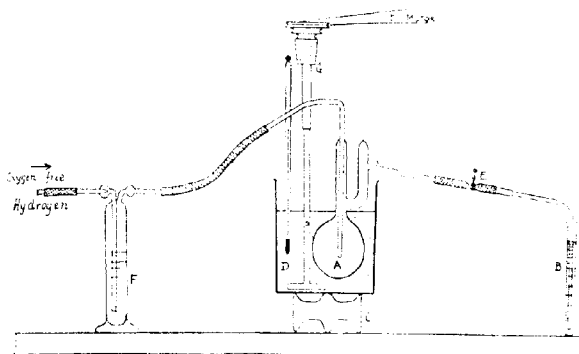
Bodenstein (*loc. cit.*), on the other hand, who repeated Pelabon's work, obtained no evidence of suspended equilibrium, the production of hydrogen sulphide from its elements proceeding normally according to a unimolecular law down to a temperature of 234° . It appears probable that the methods adopted by these two authors are open to several important errors. First, Pelabon (*Compt. rend.*, 1897, **124**, 35) has shown that molten sulphur dissolves hydrogen sulphide in quantities increasing with the temperature to which the system is heated, the gas being liberated on solidification of the sulphur. Under their conditions of experiment, this evolved gas would vitiate the results of both Bodenstein and Pelabon, being added to the equilibrium quantity of hydrogen sulphide measured after the cooling of their bulbs.

Secondly, it is uncertain from the work of Pelabon and Bodenstein whether the walls of the vessels exerted any catalytic effect. The fact that Bodenstein obtained a gradual increase in the temperature coefficient of the reaction, for example, from 1.34 between 234° and 283° to 1.77 between 310° and 356° , is not in harmony

with his conclusion that the reaction is homogeneous and confined to the gaseous phase.

In view of the possible errors inherent in the static methods adopted by the above investigators, and also as a result of experience obtained from some personal attempts at a static method, the authors came to the conclusion that a dynamic method of investigating the problem might throw new light upon it. The streaming method described below has the advantage that the same vessel can be used throughout, thus keeping surface effects constant, and is free from the error consequent upon the solution of hydrogen sulphide by molten sulphur, described above.

FIG. 1.



- | | |
|-------------------------------|------------------------------------|
| A. Reaction vessel. | E. Screw clip regulating gas flow. |
| B. Absorbing potash solution. | F. Sulphuric acid wash-bottle. |
| C. Gas ring supporting bath. | G. Stirrer. |
| D. Thermostat bath. | |

It has been found possible to show that the combination of hydrogen and sulphur takes place by way of two reactions, a gaseous and a surface reaction, the former being predominant above 285° (for the vessel employed), and the latter more important below this temperature, the temperature coefficients of the two reactions being constant, but widely different in value.

EXPERIMENTAL.

A Claisen flask of about 60 c.c. capacity was carefully cleaned with chromic acid, distilled water, and methyl alcohol, and finally dried. Into it one gram of pure sulphur was weighed, and the top of the side tubulure sealed up. Into the main tubulure a tube was sealed, passing to the centre of the flask, for the delivery of hydrogen (Fig. 1). The hydrogen used was obtained from a

TABLE I.

Pressure of hydrogen = 0.810 atm.

Rate of flow of gas = 136 c.c. per hour.

Temp.	No. of estimations.	Colorimeter reading divided by time in minutes.	Grams of H_2S formed per sec. $\times 10^3$.	Log (wt. H_2S formed per second).
265	10	0.273	1.02	-7.9914
285	14	0.884	3.31	-7.4892
305	..	4.58	17.2	-6.7645
325	10	12.9	48.1	-6.3179
340	..	41.9	157.0	-5.8041

TABLE II.

Pressure of hydrogen = 0.304 atm.

Rate of flow of gas = 136 c.c. per hour.

Temp.	No. of estimations.	Colorimeter reading divided by time in minutes.	Grams of H_2S formed per sec. $\times 10^3$.	Log (wt. H_2S formed per second).
265 ²	15	0.219	0.82	-8.0862
285	11	0.592	2.21	-7.6556
305	10	1.74	6.49	-7.1878
325	12	6.14	23.0	-6.6383
340	15	18.1	67.8	-6.1688

cylinder of electrolytic hydrogen, and was stored in a gas-holder. It was purified from oxygen by passing over a heated spiral of copper gauze and finally dried by passage through a wash-bottle containing sulphuric acid. The hydrogen was allowed to flow through the sulphur bulb, maintained at a constant temperature in a bath of the eutectic mixture of potassium and sodium nitrates. When this bath was kept well stirred, it was found possible to regulate the temperature to 0.5° . The hydrogen sulphide formed was carried forward in the gas stream and absorbed by bubbling the effluent gas through caustic potash solution.

By regulating the speed of bubbling, the rate of gas flow was kept constant. Under these conditions, when the system had attained equilibrium, the velocity of the reaction at a given temperature could be measured by estimating the hydrogen sulphide absorbed by the potash over a given interval of time. This was accomplished colorimetrically. The solution was acidified with acetic acid, and the sulphide precipitated as colloidal lead sulphide by the addition of excess of lead acetate solution. The brown tint of the solution so obtained was then compared in a colorimeter with that of a standard, freshly prepared from a solution of lead acetate containing 0.025 gram per litre.

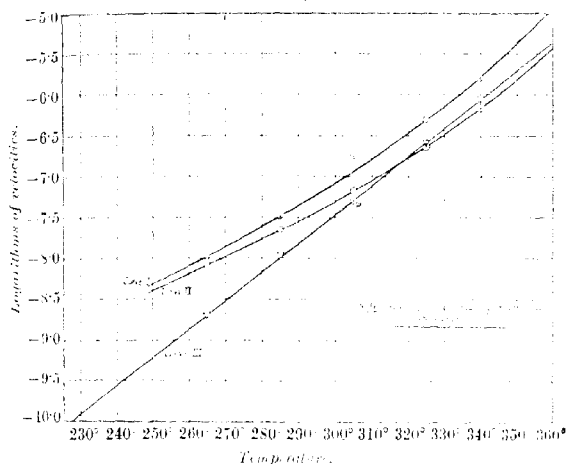
The reaction was carried out at various temperatures for two

different pressures of hydrogen, by diluting the gas with nitrogen. The results obtained are given in Tables I and II.

If the logarithms of the velocities are plotted against time (curves I and II, Fig. 2), it will be observed that straight lines are not obtained. The curvature in fact confirms Bodenstein's observations (*loc. cit.*) that the temperature coefficient of the reaction increases gradually with temperature.

If, however, we plot the logarithms of the differences of corresponding velocities for the two pressures against temperature, we obtain a straight line (curve III, Fig. 2). This fact led us to the conclusion that there are two reactions proceeding concurrently, a

FIG. 2.



surface reaction and a gaseous reaction, and that the former, assumed independent of pressure and therefore constant, disappears on taking the difference of the corresponding velocities.

Curve III thus refers to a gaseous reaction proceeding at pressure $0.810 - 0.304 = 0.506$ atmosphere. Assuming this reaction to be directly proportional to the pressure, we can obtain from it by simple proportion the velocities of the gaseous reactions at the pressures employed, that is, 0.810 and 0.304 atm. The logarithms of these velocities, plotted against temperature, give of course two straight lines parallel to curve III (curves IV and V, Fig. 3). The surface reactions at the two pressures employed can now be determined by subtracting the gaseous velocities, obtained as above,

from the corresponding observed total velocities. These, on our hypothesis, should be equal, being independent of pressure. That this is so will be seen by referring to Table III; column 2 gives the antilogarithms of points taken from curve III. In columns 3 and 4 are recorded the gaseous reaction velocities calculated from them as described above. Columns 5 and 6 give surface reaction velocities calculated from curves I and IV and from curves II and V, respectively; column 7 gives the mean surface reaction velocity.

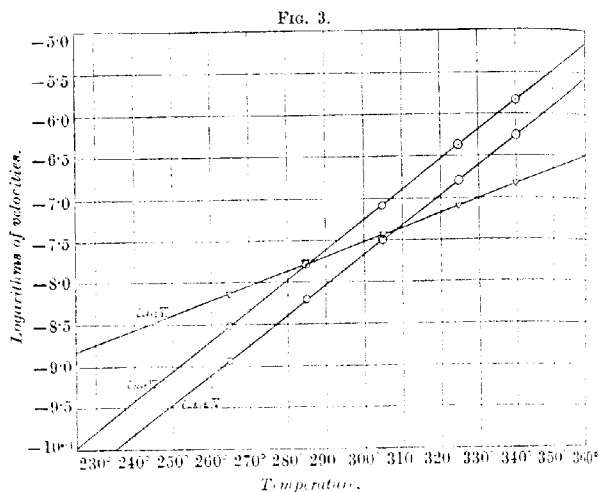


TABLE III.

Temp.	Antilogs. from curve III $\times 10^4$.	Gas react. vels. in grams per second $\times 10^4$.		Surface react. vels. in grams per second $\times 10^4$.		Mean	Logs. surface velocity.
		0.810 Atm.	0.304 Atm.	0.810 Atm.	0.310 Atm.		
265°	0.188	0.300	0.113	0.72	0.71	0.715	-8.146
285	1.00	1.60	0.60	1.71	1.61	1.66	-7.780
305	5.01	8.02	3.01	3.48	3.48	3.48	-7.458
325	25.1	40.2	15.1	7.90	7.90	7.90	-7.102
340	80.1	142.6	53.5	14.4	14.3	14.35	-6.843

Finally, it will be observed that if the logarithms of the calculated surface velocity are plotted against temperature (curve VI, Fig. 3), a straight line is obtained whose slope is less than that of the gaseous reaction. This indicates that the surface reaction has a perfectly definite and constant temperature coefficient, less than that of the gaseous reaction.

The temperature coefficients of the two reactions may be calculated from the slopes of curves IV and V and of curve VI, giving the values, gaseous reaction 2.26, surface reaction 1.48.

The fact that a straight line is finally obtained by plotting the logarithms of the surface reaction velocities against temperature is strong confirmation of the assumption adopted for dealing with the experimental curves, namely, that the gaseous reaction is proportional to the pressure, and the surface reaction independent of the pressure. The variable temperature coefficient of the reaction first observed by Bodenstein is thus a result of the combination of two reactions, surface reaction and gaseous reaction, possessing constant but widely differing temperature coefficients.

The Surface Reaction.

As a result of experiments carried out using flasks of different internal surface area, it was found possible to show that the surface action is directly proportional to the area of the internal surface of the reaction chamber, and thus independent of the quantity of sulphur present. This quantitative observation was borne out by the observation that on removing the reaction flask suddenly from the bath, the whole internal surface was covered with a thin film of liquid sulphur, which quickly solidified to a coating of feathery crystals.

Five reaction flasks of the type described above, varying in volume from 260 c.c. to 33.5 c.c., after cleaning and drying, were each charged with 1 gram of sulphur. One of the flasks (No. 4) was that used in the experiments already detailed. The flasks were then connected through calcium chloride tubes with a source of pure hydrogen at atmospheric pressure and evacuated and filled with the gas three times. They were all heated in the same oil-bath, kept well stirred at 250° for three hours. The effluent gas from each flask was passed into 60 c.c. of N 100-caustic soda solution; finally, the flasks were all allowed to cool to 150° in a current of hydrogen, the total hydrogen sulphide formed in each under identical treatment thus being collected in the respective soda solutions. The estimation was carried out colorimetrically as before; the results are given in Table IV. Columns 2, 3, 4, and 5 give the various dimensions of the flasks employed, the total internal surface being computed from the formula

$$s = 4\pi r^2 + 2\pi(r_1 + r_2)l,$$

where r is the radius of the flask, l the effective length of the hydrogen delivery tube, r_1 and r_2 the internal and the external radius of the delivery tube. Columns 6 and 7 give the surface and volume

reactions, calculated from the known surface and volume reactions in flask 4 (see curves IV, V, and VI), on the assumption that the surface reaction is proportional to the total internal surface of the vessel, and the gaseous reaction to the total volume.

TABLE IV.

Flask No.	Internal radius. Cm.	Effective length of H_2 tube.		Total surface. Sq. cm.	Total volume C.c.	Calc. surface action.	Calc. volume action.	Total calc. action.	Total observed action.
		Grams of $H_2S \times 10^3$.	Grams of $H_2S \times 10^3$.			Grams of $H_2S \times 10^3$.	Grams of $H_2S \times 10^3$.	Grams of $H_2S \times 10^3$.	
1	3.95	5.0	218	259	1.25	0.55	1.80	1.83	
2	3.45	4.0	169	172	0.97	0.36	1.33	1.35	
3	3.05	3.0	130	159	0.75	0.25	1.00	1.00	
4	2.60	2.5	95.9	73.6	0.55	0.156	0.706	0.706	
5	2.00	2.5	61.5	33.5	0.352	0.071	0.423	0.538	

The very close agreement between the calculated and observed values in columns 8 and 9 may be taken as strong proof that the surface reaction is directly proportional to the total internal surface of the reaction vessel.

In the light of the results of the present paper it is now possible definitely to assert that there are no grounds for Pelabon's contention (*loc. cit.*) that the reaction between hydrogen and sulphur shows false equilibrium between 350° and 215° . His results are simply due to the fact that he did not heat his bulbs long enough for equilibrium to be established. With the help of the curves for the surface and the gaseous reactions in Fig. 3, and knowing also, from the volumes given by Pelabon, the ratios of the surfaces and volumes of his bulbs to the surface and volume of our reaction vessel, it is possible to calculate the percentage of hydrogen sulphide which should have been formed in each, assuming the surface and volume reactions to proceed perfectly regularly according to the principles laid down above.

In Table V the calculated percentages, shown in comparison with Pelabon's experimental data, were obtained neglecting the reverse reaction of decomposition of hydrogen sulphide, which is known to be very small at the temperatures of the experiments, and also on the assumption that Pelabon filled his bulbs with hydrogen at atmospheric pressure, and sealed them at the ordinary temperature before heating.

The close parallelism between the calculated and the observed percentage of hydrogen sulphide in Pelabon's bulb is strong confirmation that the reaction therein was proceeding normally, that is, he obtained no less hydrogen sulphide than one would have

TABLE V.

Temp.	Hours of heating.	Volume of bulbs (c.c.).	Surface of bulbs (sq. cm.), calc. from volumes.	Observed percentage of H_2S at end (Pelabon).	Calculated percentage of H_2S at end.
220°	624	7.15	17.9	2.1	4.7
225	237	7.05	17.7	12.0	10.7
280	162	7.13	17.9	33.6	40.8
310	168	7.45	18.4	69.1	100
350	27	6.55	16.9	97.0	100

expected from his times of heating, and his figures thus cannot be taken as evidence of any false equilibrium existing in the bulbs.

The Reaction Kinetics of the Interaction of Hydrogen and Sulphur.

For the surface reaction to be independent of pressure, as found experimentally, it is necessary either that the surface of the sulphur is practically entirely coated with hydrogen sulphide under the conditions of the experiment, and that the observed rate of reaction is simply the rate of evaporation of hydrogen sulphide from the covered surface, or that the surface is completely covered with hydrogen and that the hydrogen molecules on the surface react, as the sulphur molecules become active, at a rate dependent only on the temperature, hydrogenation taking place and the hydrogen sulphide being removed by evaporation as quickly as it is formed.

It will be shown in a later paper on the catalytic effect of oxygen gas on this reaction that the latter assumption only is in accord with facts. From the temperature coefficients of the gaseous and surface reactions we can calculate the "critical increment" or energy of activation of the two reactions. In order to obtain the true temperature coefficient for the gaseous reaction, it is necessary to correct the velocities of formation of hydrogen sulphide at different temperatures for increasing vapour pressures of the sulphur.

Assuming the reaction takes place between sulphur atoms and hydrogen molecules, the true velocity constant of the gaseous reaction at a given temperature, t , is given by :

$$V_1 = k_1 \times C_{H_2} \times C_s$$

and that at $(t + 10)^\circ$ is

$$V_2 = k_2 \times C_{H_2} \times C'_s,$$

where C_s and C'_s represent the concentrations of sulphur atoms in the vapour at t° and $(t + 10)^\circ$, respectively. C_{H_2} refers to the

concentration of the hydrogen, V_1 and V_2 are the velocities of hydrogen sulphide formation, and k_1 and k_2 the corresponding true velocity coefficients.

Thus $k_2/k_1 = V_2/V_1 \times C_s/C'_s$. But k_2/k_1 is the true temperature coefficient, V_2/V_1 the apparent temperature coefficient (that is, 2.26 from curves IV and V, Fig. 3), and C'_s/C_s is the temperature coefficient of the increase of free sulphur atoms in the vapour. Since, at the temperatures of the experiments, practically all the sulphur vapour is in the form S_8 , and dissociation probably takes place according to the scheme $S_8 \rightleftharpoons 4S_2$, $S_2 \rightleftharpoons 2S$, we may write

$$C'_s/C_s = \sqrt{C'_s/\sqrt{C_{s_8}}} = \sqrt{P'/\sqrt{P}},$$

where P' and P are the corresponding vapour pressures of sulphur at $t + 10^\circ$ and t° .

Bodenstein (*Z. physikal. Chem.*, 1899, 29, 315) gives the following values for the vapour pressure of sulphur:

Temp.....	356	310	203	234
Press. (mm.) ...	139.5	46.7	22.1	4.51

Whence it follows that $\sqrt{P'}/\sqrt{P} = 1.033$.

Thus the true temperature coefficient of the gaseous reaction is

$$k_2/k_1 = 2.26 \cdot 1.033 = 2.19.$$

The heats of activation calculated from the temperature coefficient, 1.48, for the surface reaction, and the temperature coefficient, 2.19, for the gaseous reaction, are as follows:

Surface reaction	26,200 cal.
Gaseous reaction	52,380 ..

It will be observed that the heat of activation of the gaseous reaction is exactly double that of the surface reaction.

Viewed in the light of the activation theory of chemical action, this fact is of great interest. It would appear that exactly two quanta of active energy are necessarily absorbed in the gas reaction, to one quantum in the surface reaction. It may, however, mean that the activation of the sulphur molecules can take place in one stage or in two stages. In the gaseous reaction, before combination between sulphur atoms and hydrogen molecules can take place, the sulphur molecules must be fully activated by the absorption of both quanta. In the case of the surface reaction, however, we may suppose that the adsorbed hydrogen molecules adhere to the sulphur molecules, semi-activated by the absorption of

one quantum, leading to the formation of a surface layer composed almost completely of hydrogen molecules.

This adsorbed hydrogen is converted into hydrogen sulphide on the absorption of a second quantum of like magnitude by the sulphur atoms, and the hydrogen sulphide molecules subsequently evaporate from the surface. In the case of the surface reaction we are thus really measuring the rate of chemical action between adsorbed hydrogen, and sulphur atoms in the surface.*

Summary.

The reaction between hydrogen and sulphur at temperatures below the boiling point of the latter has been studied by a dynamic flow method, free from the errors of the methods of the earlier workers on this problem. It has been demonstrated that combination takes place by way of two reactions, a gaseous reaction proportional to the pressure of the hydrogen, and a surface reaction independent of the pressure of the hydrogen. The temperature coefficient of each reaction was obtained and found to be 1.48 for the surface and 2.19 for the gaseous reaction. The surface reaction has been shown to be directly proportional to the internal surface of the vessel and independent of the quantity of sulphur in the bulb.

The statement of Pelabon that this reaction shows false equilibrium below 350° has been proved incorrect, being founded on the error that his reaction bulbs were not heated long enough for the systems to attain equilibrium.

The heats of activation of the gaseous and surface reactions have been calculated from the temperature coefficients, namely, 52,400 and 26,200 calories, respectively, the former being exactly double the latter. It is suggested in explanation of this that the sulphur molecules can become activated in two stages.

Our thanks are due to the Board of Scientific and Industrial Research for a grant to one of us (R. G. W. N.) and assistance in defraying the cost of part of the apparatus.

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Received, February 10th, 1923.]

* It is hoped to deal more fully in a later paper with the molecular mechanism of the surface and gaseous reactions.

LXXXIII. — *Heterogeneous Equilibria between the Chlorides of Calcium, Magnesium, Potassium, and their Aqueous Solutions. Part I.*

By WILLIAM BELL LEE and ALFRED CHARLES EGERTON.

DURING the course of an investigation on the quinary system $\text{CaCl}_2\text{-MgCl}_2\text{-KCl-NaCl-H}_2\text{O}$, it became necessary to study in detail the ternary systems $\text{CaCl}_2\text{-KCl-H}_2\text{O}$, $\text{CaCl}_2\text{-MgCl}_2\text{-H}_2\text{O}$, and $\text{MgCl}_2\text{-KCl-H}_2\text{O}$.

Although a considerable volume of work closely bearing on these systems has been done, much of which was pioneer work of van't Hoff and his pupils, there appears to have been published no complete study of these ternary systems.

It is the object of the present paper to place on record the results obtained at 25° for the systems $\text{CaCl}_2\text{-MgCl}_2\text{-H}_2\text{O}$ and $\text{CaCl}_2\text{-KCl-H}_2\text{O}$ together with some remarks on the system $\text{MgCl}_2\text{-KCl-H}_2\text{O}$.

I. *The Ternary System $\text{CaCl}_2\text{-KCl-H}_2\text{O}$ at 25° .*

Data for the solubility of potassium chloride and of calcium chloride are available and, in addition, Milder found that at 7° , a solution saturated simultaneously with calcium chloride hexahydrate and potassium chloride contained 2.9 per cent. of the latter (Seidell's "Solubilities," 2nd edition, p. 89). Van't Hoff ("Zur Bildung der Ozeanischen Salzablagerungen," II, p. 11) also determined two points in the quaternary system with sodium chloride present as an additional solid phase. He found that the invariant solutions contained 4.5 and 3.5 per cent. of potassium chloride at 25° and 83° , respectively.

The results of these investigators showed that the chlorides of potassium and sodium are comparatively insoluble in saturated solutions of calcium chloride.

The main purpose of the present work was to examine the form and extent of the saturation curves in the ternary system of the pure components (sodium chloride being absent) and also to obtain some idea of the form of the saturation surfaces in the quaternary system containing magnesium chloride as an additional component.

Table I gives the analytical results together with the density and viscosity data, and a graphical representation of the results obtained is given in Fig. 1.

E and *F* denote the solubility of pure potassium chloride and of calcium chloride hexahydrate, respectively, in water (grams per

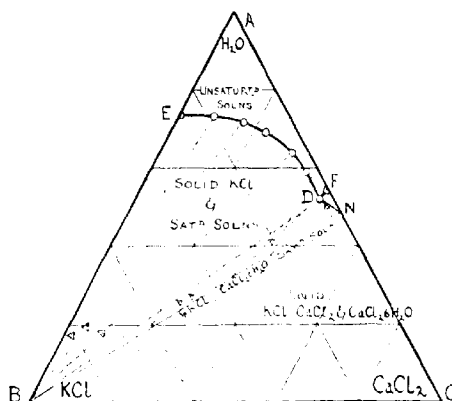
TABLE I.
The System $\text{CaCl}_2\text{--KCl--H}_2\text{O}$ at 25° .

Solid phases.	D_{25}°	Rel. viscosity.	Solutions.				Residue.			
			Grams per 100 grams of solution.				Grams per 100 grams of residue.			
			CaCl_2	KCl	H_2O		CaCl_2	KCl	H_2O	
KCl	1.182	1.072	—	26.74	73.26	—	—	—	—	—
"	1.204	1.41	8.53	17.63	73.84	—	1.92	80.95	17.13	—
"	1.236	—	16.55	11.64	71.81	—	4.32	76.33	19.35	—
"	1.273	2.685	23.15	7.52	69.33	—	—	—	—	—
"	1.349	—	32.34	3.72	63.94	—	9.00	73.00	18.00	—
"	1.602	8.11	37.82	3.15	59.03	—	—	—	—	—
KCl_2	—	—	—	—	—	—	—	—	—	—
$\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$	1.485	—	44.66	3.05	52.29	—	25.18	47.52	27.30	—
"	1.485	—	44.72	3.06	52.22	—	47.23	2.54	50.23	—
"	—	—	44.73	3.28	51.99	—	38.25	20.53	41.20	—
$\text{CaCl}_2 \cdot 6\text{H}_2\text{O}^*$	1.47	—	45.06	—	54.94	—	—	—	—	—

* Seebeck's "Solubilities," 2nd edition, 1920, p. 196.

100 grams of saturated solution). ED is the saturation curve of potassium chloride, that is, it represents the composition of all possible saturated solutions containing potassium and calcium chlorides in solution, with one solid phase present, namely, potassium chloride in contact with solution. Similarly, FD denotes the composition of the solutions saturated with respect to calcium chloride hexahydrate only. The isothermal invariant point D represents the composition of the solution saturated with respect to both potassium chloride and calcium chloride hexahydrate. The area BED is the KCl-field of complexes, and DFN is the $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ -field. Points in the area BDN represent complexes of solid potassium chloride, solid calcium chloride hexahydrate,

FIG. 1.



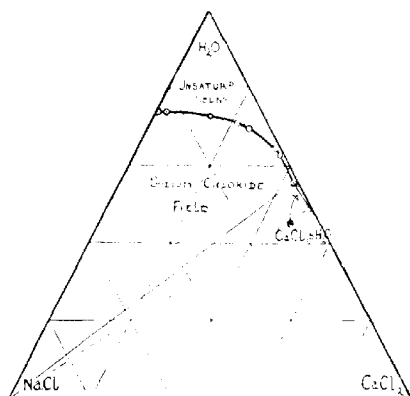
and invariant solution D . The area BNC denotes mixtures of solid potassium chloride and calcium chloride, the latter not containing sufficient water to form only hexahydrated calcium chloride. $AEDF$ is the area of unsaturated solutions.

Fig. 1 shows that the solubility of potassium chloride is relatively greatly depressed by the presence of a small concentration of calcium chloride, and that as the latter increases the potassium chloride-content rapidly decreases until it attains the order of from 3 to 4 per cent. of KCl, after which further addition of calcium chloride does not cause the percentage of potassium chloride to change appreciably. From the form of the saturation curves it is evident that if an unsaturated solution containing calcium chloride and potassium chloride is evaporated at 25° , potassium chloride will, in general, be deposited first, and further that as soon as the solution

has been concentrated to the point of crystallisation (which may vary widely according to the composition of the original unsaturated solution), potassium chloride will separate in relatively large quantity at first.

Cameron, Bell, and Robinson (*J. Physical Chem.*, 1907, **11**, 396) determined solubilities in the system $\text{CaCl}_2\text{-NaCl-H}_2\text{O}$ at 25° , and their results are plotted in Fig. 2 for comparison with Fig. 1. It is seen that the form of the saturation curves is very similar in the two systems: $\text{CaCl}_2\text{-NaCl-H}_2\text{O}$ and $\text{CaCl}_2\text{-KCl-H}_2\text{O}$, both at 25° .

FIG. 2.



Further, both potassium chloride and sodium chloride are comparatively insoluble in very concentrated calcium chloride solution, so that in the general case of the evaporation of unsaturated solutions in either of these ternary systems the bulk of the sodium chloride (or potassium chloride) will be readily recoverable.

Density Determinations.—The relative density (15°) of the monovariant solutions (KCl solid phase) may conveniently be plotted as a function of the composition (ratio CaCl_2/KCl), as it will be seen that the KCl saturation curve extends almost right across the ternary diagram. The empirical equation $\rho = 1.182 + 0.0444R - 0.0048R^2 + 0.000219R^3$, where ρ is the density and R the ratio CaCl_2/KCl , gives the density of any solution on the KCl saturation curve. The results of Cameron, Bell, and Robinson (*loc. cit.*) for the densities of the corresponding monovariant solutions in the system $\text{CaCl}_2\text{-NaCl-H}_2\text{O}$ at 25° , when plotted, give a curve which is of the same general form.

Viscosity Determinations.

The relative viscosity of solutions of pure potassium chloride at 25° passes through a minimum value with increasing concentration (compare Herz, *Z. anorg. Chem.*, 1917, **99**, 132.)

In the system $\text{CaCl}_2\text{-KCl-H}_2\text{O}$ at 25° there is a very striking increase in the viscosity of the saturated solutions with increasing concentration of calcium chloride. The effect of adding calcium chloride to a saturated solution of potassium chloride at 25.1° is to increase the viscosity until, at the "break-point," the saturated solution is more than twenty times as viscous as pure water at the same temperature.

Practical Details.—The salts used were pure potassium chloride and pure calcium chloride. The working temperature was 25.1° \pm 0.05°. The solid phases occurring in the systems investigated were characterised by the well-known "residue" method of Schreinemakers. All analyses were carried out in duplicate and in several cases the analytical work was checked by starting with a weighed complex of pure components, and after equilibrium had been reached, analysing the solution and residue. The analyses were usually carried out by precipitating calcium as oxalate and titrating the washed calcium oxalate with standard permanganate according to Peters's method (*Amer. J. Sci.*, 1901, [iv], **12**, 216), which gives results in good agreement with those obtained by the usual gravimetric method. Chlorine was estimated by titrating the neutral solution against silver nitrate. Analyses were carried out in duplicate and potassium was found by difference. A direct estimation of potassium was made at the "break-point" by the cobalt-nitrite method. Several estimations indicated that the potassium chloride content at the "break-point" was about 3.4 per cent.; the value 3.1 per cent. of potassium chloride was obtained by difference. For the relative viscosity determinations an Ostwald viscosity tube was used, the time of outflow for water being about two and a half minutes. The results given were calculated by the usual Ostwald formula. Duplicate or triplicate measurements were made.

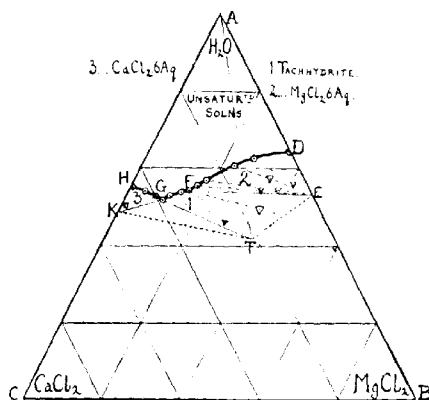
II. The Ternary System $\text{CaCl}_2\text{-MgCl}_2\text{-H}_2\text{O}$ at 25°.

Data for the solubility of the hexahydrates of calcium and magnesium chlorides separately in water are available (Seidell, Landolt, etc.). If the effect of saturation with sodium chloride be neglected, one may say that van't Hoff determined the composition of the two invariant points at 25° (*op. cit.*, II, p. 10). The results of the present work are represented graphically in Fig. 3 and in Table II.

In this system a double salt, tachhydrite, $\text{CaCl}_2\cdot 2\text{MgCl}_2\cdot 12\text{H}_2\text{O}$,

occurs and Fig. 3 also differs from Fig. 1 in that both salt components exist as stable salt hydrates at this temperature. *D* denotes the solubility of pure magnesium chloride hexahydrate in water, and *E* its composition. *H* represents the solubility of calcium chloride hexahydrate, and *K* its composition. *DF* is the saturation curve of magnesium chloride hexahydrate, *FG* and *GH* are the corresponding curves for tachhydrite and hydrated calcium chloride, respectively. *ADFGH* is the area of unsaturated solutions. The area *DEF* represents complexes of magnesium chloride hexahydrate and saturated solutions on curve *DF*, and *FGT* denotes complexes of tachhydrite + saturated solutions on curve *GF*. *EFT* is the area of complexes of solid $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ + tachhydrite + solution *F*, and

FIG. 3.



TGK the complex area tachhydrite + hydrated calcium chloride + solution *G*. *BETKC* is the area of solid mixtures of calcium chloride, magnesium chloride and water, the latter component not being in sufficient amount to form only the hydrated solid salts. The composition of the invariant solution *F* cannot be expressed in terms of positive amounts of water and the solid phases tachhydrite + $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ with which it is in equilibrium. *F* is therefore an incongruently saturated solution, and *G* denotes a congruently saturated solution.

On concentrating an unsaturated solution of the chlorides of magnesium and calcium in water, different phenomena occur according to the composition of the original solution. All unsaturated solutions lying to the right of the line *AT* will on evaporation ultimately dry up at the point *F*, and solutions on the left of this line

will dry up at the point *G*. In the former case, sufficient magnesium chloride hexahydrate will be deposited during the course of the evaporation to keep the final composition of the solution at the point *F*, and in the latter case all magnesium chloride hexahydrate deposited during the first part of the crystallisation will be redissolved owing to the phase reaction which occurs at the point *F*, where the separation of tachhydrite begins. If the magnesium chloride hexahydrate is removed as fast as it is deposited, then all unsaturated solutions on evaporation will finally dry up at the point *G*. An unsaturated solution lying in the area between *AT* and *AF* cannot deposit sufficient magnesium chloride hexahydrate during the evaporation to keep the resulting incongruently saturated invariant solution at the point *F*. This may, however, be done by adding an excess of the hexahydrate during the progress of the evaporation.

The work of van't Hoff and his collaborators has shown that tachhydrite cannot have a stable existence in contact with solution in this system at temperatures below 22°, so that an isotherm at a somewhat lower temperature than this would be of a type similar to that in the system $\text{CaCl}_2\text{--KCl--H}_2\text{O}$ at 25°, showing only one invariant point.

Van't Hoff, Kenrick, and Dawson (*Z. physikal. Chem.*, 1902, **39**, 27) found that the transition point $\text{CaCl}_2 \cdot 6\text{H}_2\text{O} \rightleftharpoons \text{CaCl}_2 \cdot 4\text{H}_2\text{O}$ (29.2°) is lowered to about 25° in the presence of tachhydrite. Consequently, at temperatures just above 25°, a very small additional field, namely, that of $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$, should appear. The present work, which was carried out at $25.1^\circ \pm 0.05^\circ$, neither disproves nor confirms the exact temperature at which calcium chloride tetrahydrate makes its appearance in this system; to establish this point by solubility measurements it would be desirable to obtain data at temperatures both appreciably above and below 25°.

Density Determinations.—The densities of the various saturated solutions occurring in this system are complex functions of the composition. The equilibria may consequently be shown graphically by plotting the density against the ratio $\text{CaCl}_2/\text{MgCl}_2$, since this ratio uniquely determines the composition of the various saturated solutions. The data are given in Table II. The density becomes a maximum when the solution is simultaneously saturated with tachhydrite and hydrated calcium chloride.

Practical Details.—Blasdale's oxalate process for the separation of calcium from magnesium (*J. Amer. Chem. Soc.*, 1909, **31**, 917) was adopted in the investigation of the system $\text{CaCl}_2\text{--MgCl}_2\text{--H}_2\text{O}$. The precipitated calcium oxalate after washing was titrated in hydrochloric acid solution in presence of a little manganous chloride according to the method of Peters (*loc. cit.*). Chlorine was estimated

TABLE II.
 The System $\text{CaCl}_2\text{--MgCl}_2\text{--H}_2\text{O}$ at 25° .

Solid phases.	D_{25}° .	Solution.			Residue.		
		Grams per 100 grams of solution.			Grams per 100 grams of residue.		
		CaCl_2 .	MgCl_2 .	H_2O .	CaCl_2 .	MgCl_2 .	H_2O .
$\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$	1.344	—	35.54	64.46	—	—	—
"	1.371	10.33	27.61	62.06	3.41	40.72	55.87
"	1.391	16.05	23.33	60.62	8.61	33.73	57.66
"	1.428	25.09	18.13	56.80	7.89	37.95	54.16
"	1.441	28.12	16.31	55.57	12.65	33.28	54.07
$\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$	1.455	31.17	14.54	54.29	15.41	33.28	49.31
tachydrate	1.460	32.82	13.55	53.63	25.10	28.60	46.30
Tachydrate	1.473	36.37	10.78	52.85	—	—	—
Calcium chloride	1.486	38.70	9.43	51.87	—	—	—
tachydrate	1.472	38.95	7.93	53.12	—	—	—
$\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$	1.465	41.87	4.06	54.07	48.82	0.98	50.20
"	1.47 *	45.06	—	54.94	—	—	—

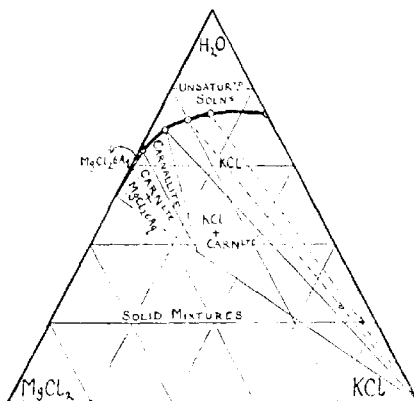
* Scheffé's "Solubilities," 2nd edition, 1920, p. 196.

by titration against silver nitrate, and occasionally tests for magnesium were made by treating the filtrate from the calcium estimation with disodium hydrogen phosphate.

III. The System $\text{MgCl}_2\text{-KCl-H}_2\text{O}$.

Although the two invariant points in this system have been determined at different temperatures by several investigators with results in good agreement, the same cannot be said in the case of the investigation of the exact form of the isothermal saturation curves. Uhlig (*Centr. Min.*, 1913, 417) has arrived at the conclusion that van't Hoff's two invariant points at 25° are slightly

FIG. 4.



incorrect. Precht and Wittgen (*Ber.*, 1881, **14**, 1667) made a series of determinations of the solubility of potassium chloride in 11, 15, 21.2, and 30 per cent. solutions of magnesium chloride which also contained some sodium chloride. Their determinations were carried out at intervals of 10° between 0° and 100° . These investigators were unaware of the fact that in the case of the 30 per cent. solution of magnesium chloride, carnallite could exist as a solid phase. Van't Hoff and Meyerhoffer (*Z. physikal. Chem.*, 1899, **30**, 84), in determining the composition of the two invariant solutions at a series of temperatures, pointed out that at all temperatures other than 10° at which these points were determined their values appear to lie on curves corresponding to a lower potassium chloride content than those of Precht and Wittgen. Feit and Przibylla (*Z. Kali*, 1909, **3**, 393) give more recent data on the solubility of potassium chloride in solutions of magnesium chloride which also

TABLE III.
The System $\text{MgCl}_2\text{--KCl--H}_2\text{O}$ at 25° .

No.	Solid phases.	D_{25}°	Solutions.			Residue.		
			Grams per 100 grams of solution.			Grams per 100 grams of residue.		
			KCl.	MgCl_2 .	H_2O .	KCl.	MgCl_2 .	H_2O .
1	KCl	1.182	26.74	—	73.26	—	—	—
2	"	1.201	13.56	12.11	74.33	75.77	3.43	20.80
3	"	1.234	7.90	16.83	72.27	68.65	6.77	54.58
4	KCl + carnallite	—	3.19	26.66	70.15	—	—	—
5	" "	—	3.20	26.79	70.01	—	—	—
6	" "	—	3.33	26.81	69.86	—	—	—
7	Carnallite +	—	0.52	35.47	64.01	—	—	—
8	$\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$	—	0.38	35.13	64.49	—	—	—
9	" "	—	0.53	35.14	64.33	—	—	—
10	$\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$	1.341	—	35.54	64.46	—	—	—

1, 2, 3, New determinations; 4 and 9, Gross, Diss., Erlangen, 1914; 5 and 8, Dehler, Diss., Erlangen, 1913; 6, D'Ans, Z. *Kali*, 1915; 7, Lowenherz, Z. *physikal. Chem.*, 1898, 12, 481; 10, New determinations.

contained sodium chloride, their results being expressed as volume percentages. No complete investigation of this ternary isotherm (sodium chloride absent) appears to have been published.

In the present work, two points on the potassium chloride saturation curve (sodium chloride being absent) at 25° were determined. These new points help to fix the form of the potassium chloride saturation surface in the solid model for the quaternary system $\text{CaCl}_2\text{-MgCl}_2\text{-KCl-H}_2\text{O}$ at 25°, and also suffice for the quantitative application of the diagram to the case of the splitting of carnallite. They have a slightly lower content of potassium chloride than the corresponding points on a curve, giving interpolated values of the results of Precht and Wittgen (*loc. cit.*), and agree more closely with the prediction of van't Hoff and Meyerhoffer.

A determination of the solubility of magnesium chloride at 25.1° gave a result rather lower than that of van't Hoff (*op. cit.*, I, p. 17), but agreeing closely with that of Biltz and Marcus (*Z. anorg. Chem.*, 1911, **71**, 187) for 25°. The solubility of pure potassium chloride was determined at 25.1°, giving as the result 26.74 per cent., in good agreement with the values of Armstrong and Eyre (*Proc. Roy. Soc.*, 1911, [A], **84**, 123; 1913, [A], **88**, 234—26.73 and 26.89 per cent.) for a temperature of 25° and with that given by Reinders (*Z. anorg. Chem.*, 1915, **93**, 202—26.46 per cent. at 25°). The solubility and the density of the saturated solution of potassium chloride were in close agreement with the values interpolated from the results of Berkeley (*Phil. Trans.*, 1904, **203**, [A], 189. The density (D_{25}°) of a saturated solution of magnesium chloride was found to be 1.341 (Table III); the addition of magnesium chloride to a saturated solution of potassium chloride causes the resulting density to increase progressively.

The curve of Precht and Wittgen does not differ greatly from the results obtained in the absence of sodium chloride.

Summary.

1. Solubilities in the ternary system $\text{CaCl}_2\text{-KCl-H}_2\text{O}$ at 25° have been determined. The diagram given represents in a complete manner the equilibria in this system. Viscosity and density data are also given.

2. Similarly, the system $\text{CaCl}_2\text{-MgCl}_2\text{-H}_2\text{O}$, in which the double salt, tachhydrite, occurs, has also been studied at 25°.

3. The system $\text{KCl-MgCl}_2\text{-H}_2\text{O}$ is discussed and new points determined which render the data for this system more complete.

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OXFORD.

[Received, January 22nd, 1923.]

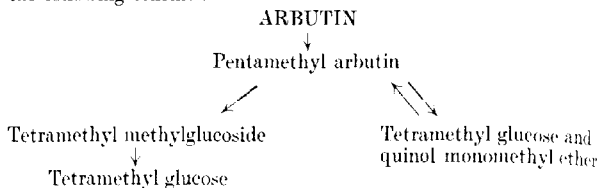
LXXXIV.—*Studies of the Glucosides. Part II. Arbutin.*

By ALEXANDER KILLEN MACBETH and JOHN MACKAY.

IN a previous paper (Macbeth and Pryde, T., 1922, **121**, 1660), it was pointed out that the complete study of the constitution of a glucoside involves the consideration of three points, namely, (a) the identification of the constituent sugar and the determination of the group of the non-sugar residue with which it is combined, (b) the determination of the configuration of the glucoside, that is, whether it belongs to the α - or β -series, and (c) the detection of the nature of the internal linking of the component sugar. The question of configuration is conveniently determined by the study of enzyme action, emulsin being the specific enzyme for the hydrolysis of β -glucosides. The other points in the study of the glucoside are most readily settled by complete methylation of the compound and examination of the products obtained on hydrolysis of the methylated derivative. Such work was previously carried out in the case of indican, and the results obtained in the study of arbutin are now recorded.

Although arbutin was early isolated from natural sources and identified as a glucoside (Schiff, *Gazzetta*, 1881, **11**, 99; Michael, *Ber.*, 1882, **14**, 2097), a considerable amount of doubt regarding its constitution existed for some time. Habermann (*Monatsh.*, 1884, **4**, 753) asserted that arbutin is a complex glucoside having the composition $C_{25}H_{31}O_{11}$, but others believed that the complexity is due to the glucoside occurring in nature as a mixture of true arbutin and its monomethyl derivative. The correctness of the latter view was established by a study of the molecular weights of samples of arbutin from different sources (Bourquelot and Hérissé, *Compt. rend.*, 1908, **146**, 764), and it was shown that the results obtained were nearly in accordance with the value 272, the figure for the glucoside of quinol. The glucoside occurs in the leaves of all the varieties of pear tree examined (Bourquelot and Fichtenholtz, *Compt. rend.*, 1911, **153**, 468), and it is also obtained from the leaves of the bearberry. The arbutin from the latter source always contains a quantity of methyl arbutin, the amount varying from 5 to 40 per cent., the purest samples being obtained from the leaves of the Spanish bearberry (Tunmann, *Chem. Zentr.*, 1907, i, 196). Various methods of obtaining arbutin free from admixture with its methyl derivative have been described (Hérissé, *J. Pharm. Chim.*, 1910, [vii], **2**, 248), but of these Mannich's treatment alone is found to be satisfactory (*Arch. Pharm.*, 1912, **250**, 547).

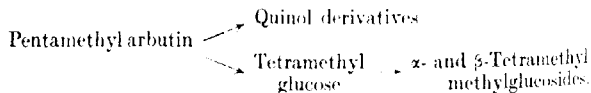
Arbutin is readily hydrolysed by dilute mineral acids and by emulsin, the products of the reaction being glucose and quinol. The behaviour towards emulsin, coupled with the optical properties of the glucoside, indicates that the compound is a derivative of β -glucose. The hydrolysis, however, affords no proof of the internal linking of the sugar, but this question is settled by the results now submitted. The work described in the paper may be outlined in the following scheme :



If the sugar residue in arbutin has the normal butylene-oxide structure, the tetramethyl glucose isolated from it should be the well-known 2:3:5:6-compound, which is crystalline and may be readily identified. If any alternative linking is present in the constituent sugar, an isomeric tetramethyl glucose would result, from which the structure of the sugar molecule might be deduced.

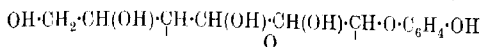
The methylation of the glucoside was accomplished by means of methyl sulphate and sodium hydroxide. In this way, pentamethyl arbutin was obtained in characteristic, white needles, melting at 75.5° and showing levorotation in all the solvents examined. Pentamethyl arbutin behaves as a normal methylated glucoside, and has no reducing action on Fehling's solution.

The hydrolysis of pentamethyl arbutin was carried out by the action of methyl alcohol containing 1 per cent. of hydrogen chloride. This method was adopted in view of the fact that previous work on the hydrolysis of methylated glucosides showed that dilute aqueous acid is, as a rule, not a suitable reagent, for the hydrolysis is slow and, in addition, considerable resinification often takes place (Irvine and Rose, T., 1906, 89, 814; Macbeth and Pryde, *loc. cit.*). The method adopted results in the hydrolysis of the glucoside and the simultaneous formation of the corresponding methylglucosides according to the scheme :



The hydrolysis proceeded normally, and the mixture of tetramethyl methylglucosides was submitted to further hydrolysis by the action

of an 8 per cent. aqueous solution of hydrochloric acid. A crystalline tetramethyl glucose was isolated from the product of this reaction, and was identified as the 2:3:5:6- or butylene-oxide compound. From the results recorded it is evident that arbutin is derived from a molecule of *d*-glucose combined with quinol, the internal linking of the sugar being of the butylene-oxide type; and therefore the following structure is established for the glucoside:



This structure is further supported by the synthesis of a pentamethyl arbutin from quinol monomethyl ether and tetramethyl glucose. The condensation was effected by heating equivalent amounts of the starting materials in benzene in a sealed tube, and the synthetic compound was found to be identical with the pentamethyl arbutin prepared from the natural glucoside by methylation.

The optical properties of the methylated glucosides have a direct bearing on the views of sugar structure expressed by Anderson (*J. Physical Chem.*, 1916, **20**, 269), and a brief reference to the question may not be out of place here. The structures proposed are arrived at from the consideration of the relation between the configuration of the sugars and their specific rotations. A review of the optical properties of the sugar-acid lactones shows that in these cases the direction of rotation is apparently determined by the position of the hydrogen atom and of the hydroxyl group attached to the γ -carbon atom; and, in general, it would appear that the sugar-acid lactones which have the ring on the same side of the structure rotate in the same direction. If sugars have also a 5-atomic lactone, or butylene-oxide, structure, the relations observed in the case of the acid lactones might be expected; and since such considerations are found to lead to contradictory results, Anderson proposes a propylene-oxide, or 4-atomic lactone structure, for the α -hexoses and pentoses. The ring in sugars which show similar specific rotations is on this formulation found to lie on the same side of the structure. Anderson further proposes an ethylene-oxide linking, or 3-atomic lactone structure, for β -glucose and other β -sugars and their glucosides. He is of opinion that the differences observed in the values of the rotations of the α - and β -forms of the sugars cannot be satisfactorily accounted for merely by a spatial difference of the hydrogen atom and the hydroxyl group attached to the terminal carbon atom. This, and the difference in stability noted in the case of the α - and β -forms of the sugars, lead to the ethylene-oxide formulation of the β -compounds.

The results obtained in the study of the alkylated glucosides are

totally opposed to any such difference in structure in the internal linkings of the α - and β -forms of the sugars. Salicin and arbutin may be selected as typical cases, and their specific rotations and the optical values of their pentamethyl derivatives are given below:

Salicin	— 50.3° (in dilute ethyl alcohol).
Pentamethyl salicin	— 52.15° (in methyl alcohol).
Arbutin	— 60.3° (in water).
Pentamethyl arbutin	— 48.2° (in ethyl alcohol).

From the values given above, it is evident that the methylated glucosides exist in the same stereoisomeric form as the parent glucosides, all being derivatives of β -glucose. If an ethylene-oxide structure is present in the β -glucosides, as suggested by Anderson, it must also be present in the pentamethyl compounds. On hydrolysis of the methylated compounds, no change in the internal linking can take place, and since it has been shown that the product of hydrolytic action is a methylated glucose of the butylene-oxide type, the 3-atomic and 4-atomic lactone structures proposed are untenable.

The assumption of a difference in the internal linking in the α - and β -forms of a sugar is further contradicted by the fact that the same tetramethyl glucose is obtained on the hydrolysis of tetramethyl methylglucoside, irrespective of the proportions of α - and β -forms present in the original glucoside (Purdie and Irvine, T., 1904, **85**, 1062, and subsequent papers).

EXPERIMENTAL.

Isolation of Pure Arbutin from the Natural Glucoside.

It is well known that the natural glucoside always contains a proportion of methyl arbutin, the quantity present depending on the source. Hérissé (loc. cit.) outlined a method of treatment which he claimed yielded a pure arbutin free from admixture with the methyl derivative. On subjecting samples of the natural glucoside to this treatment, we found that the product still contained a considerable quantity of methyl arbutin, and repetition of the process did not give a product free from the methyl derivative. Purification is best carried out by the methods proposed by Mannich (loc. cit.) either by precipitation of the arbutin as the additive product with hexamethylenetetramine, or by acetylation of the natural glucoside and fractional crystallisation of the mixed acetates. A product is thus obtained which contains no methoxyl, and has a specific rotation in water of $[\alpha]_D^{20}$ — 60.5°, for $c = 1.213$.

Methylation of Arbutin. Pentamethyl Arbutin.

As the ultimate object of the work was to obtain a fully methylated arbutin for hydrolysis, it was unnecessary to remove the methyl arbutin from the sample of the glucoside examined. This contained nearly 20 per cent. of methyl arbutin, and was subjected to methylation by methyl sulphate in the usual way. During methylation, the mixture was maintained at 30–35° and stirred vigorously. After the addition of the reagents was complete, the temperature was raised to 100° and maintained there for upwards of half an hour. On cooling the reaction mixture, part of the methylated arbutin was precipitated, methylation of the phenolic hydroxyl group having greatly decreased the solubility of the glucoside in aqueous alkaline media. After methylation, a stream of carbon dioxide gas was passed through the cold reaction mixture for two hours, and most of the alkali then precipitated as sodium carbonate by adding an excess of 95 per cent. alcohol and passing carbon dioxide for another hour. After standing for some time, the sodium carbonate was filtered and washed well with alcohol, the filtrates were neutralised with dilute sulphuric acid, and the liquid was distilled off under reduced pressure, a little barium carbonate being present to ensure neutrality. The residue, after drying in a vacuum, was treated with cold chloroform to extract the methylated product. A further quantity of the methylated arbutin was obtained by extracting the dry sodium carbonate residues with the same solvent. After removal of the greater part of the chloroform by distillation, the residue was heated under reduced pressure for some time, and the syrup so obtained extracted with ether. On removal of the latter solvent, a faintly brown syrup was obtained which crystallised after a time. Yield 19.5 grams. The product consisted of arbutin methylated beyond the trimethyl stage [Found: OMe = 32.5. $C_{12}H_{13}O_4(OMe)_3$ requires OMe = 29.0; $C_{12}H_{12}O_3(OMe)_4$ requires OMe = 37.8 per cent.]. The product was still levorotatory, but the value was lower than that of arbutin itself. In chloroform, $[\alpha]_D^{25} = -54.59^\circ$, for $c = 1.85$.

The syrup was subjected to a further methylation, the method of treatment and extraction being similar to that already described. In this way a syrup was obtained which solidified on the removal of the last traces of solvent. After crystallisation from dilute alcohol, the substance was obtained as feathery needles, of a faint brown colour. Methylation had now practically reached the pentamethyl stage [Found: OMe = 43.3. $C_{12}H_{11}O_2(OMe)_5$ requires OMe = 45.32 per cent.]. Yield 18 grams.

After four crystallisations from dilute alcohol, the product was

obtained as white, feathery needles, melting at 75.5° . The compound was still levorotatory, the value in chloroform being $[\alpha]_D^{25} = -40^{\circ}$ ($c = 1.556$).

On account of the low Zeisel result obtained with the above material, and in order to ascertain if the substance was fully methylated, 9 grams of the product were subjected to the methylating action of methyl iodide and freshly prepared silver oxide. No extraneous solvent was required in the reaction, as the methylated arbutin was soluble in the methyl iodide. After methylation, the methyl iodide was distilled off, and the residue treated with chloroform in a Soxhlet extractor. On removal of the chloroform, the product was subjected to another methylation, and the chloroform solution was in this case decolorised by the addition of a little vegetable charcoal (norit) during extraction. After filtration and removal of the solvent, 8.5 grams of methylated product were obtained, which crystallised from aqueous alcohol in characteristic, white, feathery needles melting at 75.5° . Analysis shows that the substance is *pentamethyl arbutin*, and the silver oxide methylation has had no appreciable effect on the product obtained after two methylations with methyl sulphate [Found: C = 59.69; H = 7.76; OMe = 44.5. $C_{12}H_{11}O_2(OMe)_5$ requires C = 59.65; H = 7.6; OMe = 45.32 per cent.].

Pentamethyl arbutin is very soluble in acetone or ether, easily soluble in alcohol, chloroform, or benzene, and difficultly soluble in cold water. It crystallises from dilute alcohol without water of crystallisation, and is levorotatory in all the solvents examined (in acetone, $[\alpha]_D^{25} = -43.2^{\circ}$ for $c = 1.736$; in ethyl alcohol, $[\alpha]_D^{25} = -48.2^{\circ}$ for $c = 2.112$; in chloroform, $[\alpha]_D^{25} = -41^{\circ}$ for $c = 1.610$).

Synthesis of Pentamethyl Arbutin.

Additional support for the view that arbutin is derived from the butylene-oxide type of glucose is furnished by the synthesis of a pentamethyl arbutin identical with that obtained by methylation of the natural glucoside. A 6 per cent. solution of tetramethyl glucose in dry benzene, containing about 0.25 per cent. of hydrogen chloride, was heated with the equivalent quantity of quinol mono-methyl ether in a sealed tube for twenty-seven hours at 110° , a little anhydrous sodium sulphate being present. When cold, the reaction mixture was neutralised with silver carbonate and, after filtration, the benzene distilled off under reduced pressure, the last traces being removed by the successive addition and removal under reduced pressure of absolute alcohol. The brown, non-reducing syrup thus obtained was treated with water to remove any octamethylglucosido-glucosides formed during the reaction.

The residual oil consisted of a mixture of unchanged quinol mono-methyl ether and pentamethyl arbutin. The methylated glucoside was best isolated by shaking the oil with a dilute solution of sodium hydroxide and ether. The ethereal extract was separated, the ether evaporated, the residue dissolved in a little boiling alcohol, and hot water added until a cloudiness just appeared. Crystallisation set in on cooling and pentamethyl arbutin was obtained in the form of the characteristic needles. It was contaminated with a brown impurity, but after four crystallisations from aqueous alcohol it was obtained in beautiful, white needles, identical with those derived from the natural glucoside by methylation. The synthetic substance melts at 75.5° , alone or mixed with a specimen of the compound prepared by methylation. It has $[\alpha]_D^{20} = -41^{\circ}$ in chloroform ($c = 1.712$). Yield, 10 per cent. of the theoretical amount.

Simultaneous Hydrolysis and Condensation of Pentamethyl Arbutin.

The hydrolysis of pentamethyl arbutin was accomplished by the action of a methyl-alcoholic solution of hydrogen chloride, and the component sugar of the glucoside isolated from the product of reaction as the tetramethyl methylglucoside. Four grams of pentamethyl arbutin, prepared by methylation of the glucoside as already described, were dissolved in 60 c.c. of dry methyl alcohol containing 1 per cent. of hydrogen chloride, and the solution was heated in a sealed tube for twenty-four hours. The temperature was kept at 80° for the first twelve hours and was then gradually raised to 120° and maintained at the latter temperature for a further twelve hours. The reaction mixture, which was somewhat coloured, was neutralised with silver carbonate, and the alcohol removed under reduced pressure. The aqueous extract of the residual syrup was boiled with a little vegetable charcoal and filtered, the solvent removed, and the residual syrup dried by successively adding and distilling off small quantities of alcohol. The syrup was finally extracted with ether and the extract dried with anhydrous sodium sulphate. The residue obtained after filtering and removal of the solvent was distilled, and 2.3 grams of a pale yellow syrup, b. p. $105-110^{\circ}$ 0.2 mm., were collected (Found: OMe = 58. Tetramethyl methylglucoside requires OMe = 62 per cent.).

The methoxyl content shows that the product consisted mainly of tetramethyl methylglucoside, but some tetramethyl glucose which had escaped glucoside formation was also present. The conversion into the glucoside was completed by subjecting the product to methylation by methyl iodide and silver oxide, and after isolating the product in the usual way a practically colourless syrup was

obtained on distillation (Found: OMe = 60.9 per cent.). Conversion into the glucoside was therefore complete.

A further quantity of pentamethyl arbutin was hydrolysed by dissolving 7 grams of the methylated glucoside in 140 c.c. of dry methyl alcohol containing 1 per cent. of hydrogen chloride. A little vegetable charcoal was present to prevent the development of colour. The levorotation of the solution gradually decreased and after five hours the solution (1-dem. tube) showed $\alpha = +4.2^\circ$, which remained constant on further heating under reflux for an hour. After neutralisation, a syrup was isolated as described in the preceding case. It consisted mainly of tetramethyl methylglucoside and distilled at $108-110^\circ/1.2$ mm. Yield 3.5 grams. No further methylation was carried out in this case, and the product was submitted to further hydrolysis forthwith.

Hydrolysis of Tetramethyl Methylglucoside.

The two specimens of tetramethyl methylglucoside obtained in the above hydrolyses were submitted to the action of aqueous 8 per cent. hydrochloric acid in different experiments, and tetramethyl glucose of the butylene-oxide type was isolated in both cases (compare Macbeth and Pryde, *loc. cit.*).

After one crystallisation from light petroleum, the sugar melted at 82° , and subsequent recrystallisation raised the melting point to 94° , the change of melting point being characteristic of tetramethyl glucose. The tetramethyl glucose showed the customary mutarotation in water, the values observed being $+91^\circ \rightarrow +83.4^\circ$, which are in good agreement with those established for the compound.

It is therefore evident that the sugar resulting from pentamethyl arbutin is tetramethyl glucose of the butylene-oxide type, and it follows that in the parent glucoside the component sugar possesses a linking of this type.

We wish to express our thanks to Principal Irvine for the interest he has taken in this work throughout, and to the Carnegie Trust for a scholarship which enabled one of us to participate in the research.

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[Received, February 12th, 1923.]

LXXXV.—*Co-ordination Compounds and the Bohr Atom.*

By NEVIL VINCENT SIDGWICK.

SOME ten years ago Werner * succeeded in resolving certain of his co-ordinated compounds into their optically active components, and thereby definitely established the truth of his view of their sixfold structure. Since then, structural chemistry has been in the unsatisfactory condition of having two incompatible theories, that of the organic chemist, and that of Werner, each quite competent to explain the relations of its own group of substances, but neither capable of being extended with any success to cover the whole field. It was obvious that it must ultimately become possible to apply one set of principles to the elucidation of the structure of both classes of compounds; and the object of this paper is to show that with the help of Bohr's † recently published theory of atomic structure this can now be done.

Werner applies his doctrine very widely; but if we limit ourselves to those co-ordinated compounds whose structures in solution have been determined by the observation of optical activity, geometrical isomerism, or ionisation (or all three), we cannot doubt the correctness of his conclusions. The peculiarities of these substances are of two kinds. There is first the peculiar co-ordination number, which determines the number of groups attached to the central atom of the complex: this is most commonly 6, but sometimes 4, and other numbers are also suggested. We may confine our attention for the moment to those in which it is 6: a fourfold structure is already familiar to us among organic compounds. The second point is the constitution of this sixfold complex, which seems to defy the laws of valency, since one univalent radicle can replace a whole molecule of water or ammonia without disturbing the structure.

To explain the first point, the sixfold structure, we must consider in outline Bohr's theory as to the relation of the groups in the periodic table. Bohr regards the electrons as rotating round the nucleus in orbits whose shapes are determined by the laws of ordinary dynamics, but subject to the quantum restriction, which makes a certain set of orbits alone possible. Each orbit is defined by two quantum numbers, the meaning of which may be roughly

* "Neuere Anschauungen auf dem Gebiete der anorganischen Chemie," 1913. The reference throughout this paper is to this book: more detailed references seem unnecessary.

† "The Theory of Spectra and Atomic Constitution," 1922.

expressed by saying that, so far as we can regard the orbit as an ellipse, the first number represents its major axis, and the second its latus rectum; so that if they are equal the orbit is circular, and the more they differ, the greater its eccentricity. The arrangement of the orbits in an atom is arrived at by means of Bohr's correspondence principle, resting on a mathematical analysis of possible orbits, and is largely supported by the evidence of the optical spectra.* The arrangements in different atoms differ in stability. Chemical combination depends solely on the possibility of increasing this stability by a rearrangement of the orbits through the co-operation of two or more atoms. In the inert gases we have electronic systems of such symmetry that their stability cannot be thus increased: hence the inactivity of these gases. The effect of chemical combination is to approach this symmetry, either by the "sharing" of electrons so that they count for both atoms (non-polar linkage, covalency) or through an electron passing over from one atom to the other (polar linkage, electrovalency).

The atomic numbers of the inert gases tell us the size of the successive groups of electrons which lead to structures of maximum stability. The position of these groups in the Bohr atom differs from that assumed by Lewis and Langmuir in that the larger groups are not on the outside but in the middle. The number of electrons in each type of orbit in the inert gases is given by Bohr in the following table:

Orbits.....	1 ₁	2 ₁	2 ₂	3 ₁	3 ₂	3 ₃	4 ₁	4 ₂	4 ₃	4 ₄	5 ₁	5 ₂	5 ₃	6 ₁	6 ₂
At.No.															
Helium	2	2													
Neon	10	2	4	4											
Argon	18	2	4	4	4	4									
Krypton	36	2	4	4	6	6	6	4	4	4	—				
Xenon	54	2	4	4	6	6	6	6	6	6	—	4	4	—	—
Radon	86	2	4	4	6	6	6	8	8	8	8	6	6	6	4

The development of these groups takes place in three different ways. There is first that of an s-group: this is illustrated by the first short period of the periodic table: it has a double fourfold symmetry; from Li 3 to C 6 we have four orbits of 2₁, followed (N 7 to Xe 10) by four of 2₂. This method of growth repeats itself in the second short period (Na 11 to A 18): in the second half of each of the two long periods (Ca 20 to Kr 36, and Ag 47 to Xe 54), and finally in the last quarter of the fifth period (Au 79 to Hg 80). A second form of development occurs in the first half of the two long periods, or rather just after their beginning (Sc 21 to Ni 28, and Y 39 to Pd 46), and in the third quarter of the fifth period.

* It is also entirely confirmed by the X-ray spectra (Bohr and Oster, *Z. Physik*, 1923, **12**, 342).

from about Lu 71 to Pt 78. In each of these there are in the outer group of electrons two sub-groups of 4 developing into 3 of 6; this involves 10 elements instead of 8, and so the single inert gas is replaced by one of the three triads of Mendeléeff's eighth group. (The rare-earth group, with which we are not concerned, is due to the development of 3 sub-groups of 6 into 4 of 8, giving 14 rare-earth metals.)

Thus, in carbon and nitrogen and their analogues, we are dealing with atoms which have a group of 4 valency electrons already established, and which seek to complete their symmetry by forming a second group of 4, as in the inert gases. This they do by "sharing" electrons with other atoms, carbon, for instance, forming methane, and thus completing their "octets." How this sharing is accomplished we do not know for certain; but since Prof. Nicholson has found that it is only possible to derive the spectrum of molecular hydrogen on the supposition that each electron encircles both nuclei, we may reasonably assume that in methane the electron of each hydrogen atom goes round the carbon nucleus as well, giving the same kind of stable arrangement of 8 orbits that we find in neon. Moreover, as Bohr has shown that the planes of the four orbits in carbon are parallel to the faces of a tetrahedron, the tetrahedral symmetry is attained which the stereochemistry of carbon requires.

In those parts of the table where the outermost group of electrons is building up sub-groups of 6 and not of 4, we may expect quite different relations. The elements in these neighbourhoods have very remarkable properties. They all form metallic ions with variable valency, with marked colours, and with pronounced paramagnetic power; and they are elements of high catalytic activity. Now it is precisely to these groups that all the well-established co-ordinated compounds (with the number 6) of Werner belong (Cr, Fe, Co, Ni; Rh; Os, Ir, Pt). The exact disposition of the orbits is here uncertain, and their stability is less than that of the fourfold groups, as is shown most conspicuously by the fact that nickel, palladium, and platinum are not inert gases. But it is clear that as when the valency orbits are arranged in fours fourfold structure develops in the molecule, so when they are in sixes sixfold structure should be exhibited. In fact the familiar "octet" theory does not apply to the elements in these neighbourhoods: the octet is replaced by a group of 12 shared electrons, which is expressed by the Werner co-ordination number of 6; and the stereochemical results show that these 6 groups of atoms are arranged at the angular points of an octahedron.

The number 6 is thus explained. The second peculiarity of

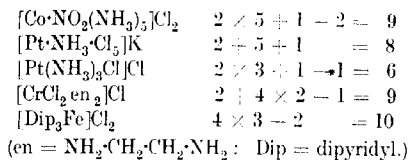
these co-ordinated compounds, the apparent equivalence of univalent radicles and molecules of ammonia or water, as well as their behaviour on ionisation, can easily be accounted for on the ordinary principles of structural chemistry. It is well known, and the point has been emphasised by Langmuir, that the valency of the atoms in the three periodic groups following that of carbon is increased by one when they become positively charged (that of the three groups preceding carbon increases in the same way by one when they become negatively charged). Thus the neutral nitrogen atom has 5 valency electrons; if it combines with three hydrogen atoms, its octet is made up and it is in a sense saturated. A nitrogen atom which has expelled an electron (and thus acquired a positive charge) has 4 valency electrons, and closely resembles the neutral carbon. It can now take up 4 univalent groups to form an ammonium ion. In the same way, while the neutral oxygen atom is bivalent, positively charged oxygen can form three non-polar linkages, giving an oxonium-ion. Now if we take one of Werner's series, such as the platinumic, we find at one end a compound, $[\text{Pt}(\text{Cl})_6]\text{K}_2$, with a bivalent anion. The chlorine atoms can be replaced one by one by ammonia (or water) groups. Every such replacement reduces the negative charge on the group by one unit, so that $[\text{Pt}(\text{NH}_3)_2\text{Cl}_4]$ is a neutral, non-ionised molecule. Further replacements give the group an increasing positive charge, until finally we arrive at $[\text{Pt}(\text{NH}_3)_6]\text{Cl}_4$, where the complex ion has 4 positive charges. This is just what the structural theory requires. The 6 groups in the bracket (whether Cl or NH_3) are all attached by single non-polar linkages to the platinum. The nitrogen is thus quadrivalent, being, in fact, a substituted ammonium, with all the rest of the complex as the substituent. In order to assume this form, it must expel an electron, and thus every time a chlorine atom is replaced by NH_3 , the complex gains one positive charge. This reaction is already familiar in organic chemistry; for example,

$$\left[\begin{array}{c} \text{H} > \text{C} < \text{H} \\ | & & | \\ \text{H} & & \text{Cl} \end{array} \right] \longrightarrow \left[\begin{array}{c} \text{H} > \text{C} < \text{H} \\ | & & | \\ \text{H} & & \text{NH}_3 \end{array} \right]^+ \text{Cl}^-$$
 The same thing happens with water, which requires to lose an electron in order to form a new non-polar linkage. The equivalence of the radicles and the whole molecules is thus only apparent. They both have the same relation (a single link) to the central atom; but one can only replace the other if a corresponding change takes place in the charge on the complex; and this change is found experimentally to occur.*

We can therefore determine the effective valency of the central

* Since this was written, I find that Ramsay gave a very similar explanation of this replacement in his Presidential Address in 1908 (T. 93, 785).

atom—that is, the number of electronic orbits which it gains from the attached groups—in the following way. Every NH_3 or H_2O will contribute two electrons, one for the linkage, and one extra to make the nitrogen or oxygen quadri- or ter-valent. Each Cl or other univalent radicle will add one, for the linkage. Each (uni-valent) kation outside the bracket will also add one, whilst for every anion one must be subtracted. (Extensions of these principles are obvious: CO_3 or $\text{C}_2\text{O}_4 = +2$, $\text{NH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NH}_2 = +4$, etc.) In this way, for every co-ordinated compound the ionisation of which is established, we can arrive at a number expressing the effective valency of the central atom. One or two examples may be quoted:



If this method is applied to all the co-ordinated compounds of ascertained structure, we get consistent values for each series, which are given in the table below. To obtain from these the actual number of valency electrons, or electrons in the two highest quantum groups, in the saturated atom, we subtract from the atomic number the number of electrons in the lower quantum groups (for the Fe series $2 + 8$, for the Pd series $2 + 8 + 18$, for the Pt series $2 + 8 + 18 + 32$) and add to the difference the valency number calculated from the compound. The results are given in the following table, the compounds with a co-ordination number of 6 being separated from those of 4. The first column gives the number of electrons in the two highest groups of the isolated atom, the second the effective valency of the compounds, and the third the sum. Doubtful values are enclosed in brackets.

Co-ordination Number 4.									
Cr	14	9	23	Rh	17	9	26	Os	16 (10 26)
Fe	16	10	26					Ir	17 9 26
Co	17	9	26					Pt	18 8 26
Ni	18	(10 28)							
Co-ordination Number 6.									
Ni	18	(6 24)		Pd	18	6	24	Pt	18 6 24
								Au	19 5 24

The following list gives some of the very numerous compounds from which the values in this table are obtained (R = kation, X = anion, Py = pyridine):

Co-ordination number 6 : $[\text{CrCl}_2\text{en}_2]\text{X}$, $[\text{Cren}_3]\text{X}_3$,
 $[\text{CrOH}\cdot\text{H}_2\text{Oen}_2]\text{X}_2$, $[\text{Fe}\cdot\text{Dip}_3]\text{X}_2$, $[\text{Fe}(\text{C}_6\text{H}_5\text{NC})_6]\text{X}_2$, $[\text{Co}(\text{NO}_2)_3(\text{NH}_3)_3]$,
 $[\text{CoNO}_2\cdot\text{C}_2\text{O}_4(\text{NH}_3)_3]$, $[\text{CoCl}\cdot\text{NH}_3\text{en}_2]\text{X}_2$, $[\text{Ni}\cdot\text{en}_2]\text{X}_2$, $[\text{Ni}(\text{NH}_3)_6]\text{X}_2$,
 $[\text{Rh}\cdot\text{en}_3]\text{X}_3$, $[\text{Rh}(\text{C}_2\text{O}_4)_3]\text{R}_3$, $[\text{Rh}\cdot\text{H}_2\text{O}(\text{NH}_3)_5]\text{X}_3$, $[\text{Os}\cdot\text{O}_2(\text{NO}_2)_4]\text{R}_2$,
 $[\text{Ir}\cdot\text{OH}\cdot\text{H}_2\text{O}(\text{C}_2\text{O}_4)_2]\text{R}_2$, $[\text{Ir}(\text{OH})_2(\text{C}_2\text{O}_4)_2]\text{R}_3$, $[\text{Pt}(\text{NH}_3)_6]\text{Cl}_4$, $[\text{PtCl}_6]\text{R}_2$,
 Co-ordination number 4 : $[\text{Ni}\cdot\text{en}_2]\text{X}_2$, $[\text{Pd}(\text{NH}_3)_4]\text{X}_2$, $[\text{PdCl}_4]\text{R}_2$,
 $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$, $[\text{Pt}(\text{NH}_3)_2\text{Py}_2]\text{X}_2$, $[\text{AuCl}_4]\text{R}$.

With the exception of chromium (and possibly nickel, where, however, the number of compounds available is small) the agreement is remarkable; and it is to be noticed that 26 is the number of electrons (3 sub-groups of 6 and 2 of 4) which we find in the next higher inert gas, just as in methane the carbon atom has the same number of electrons as neon; the disposition of the attached groups is, however, governed by the structure of the 6 sub-groups, and not by that of the 4. •

The compounds of co-ordination number 4 (which do not seem to be formed before the third member of the triad is reached) have uniformly two electrons less than this. In the case of platinum, Werner has shown that these 4 atomic groups are not arranged as in carbon, but in a plane, since compounds of the type Pt_2B_2 occur in two geometrically isomeric forms. [The same relations were found by Vernon (T., 1920, 117, 86, 889) to hold with tellurium, in compounds of the type $\text{Te}(\text{CH}_3)_2\text{I}_2$.] This suggests that the octahedral symmetry is still maintained, the two groups at the end of a diagonal being absent.

The results given above represent the most thoroughly investigated of the co-ordinated compounds of these metals. Among the less well-known, many other types will be found, and in view of the changing valency of the simple metallic ions this is to be expected. In particular, the complex cyanides show quite a different kind of regularity, the types R_2XCy_6 and R_4XCy_4 prevailing, irrespective of the atomic number of X; this makes it probable that in these cases the number 6 is due to some wholly different cause, such as the formation of tricyanogen rings. But the evidence adduced is enough to show that the structure of those compounds for which Werner's doctrine of sixfold symmetry is most fully established can be explained, with the help of Bohr's theory, on the principles which have proved so successful in organic chemistry.

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Received, February 15th, 1923.

LXXXVI.—*The Hydrogen Sulphates of the Alkali Metals and Ammonium.*

By HORACE BARRATT DUNNICLIFF.

It has been stated (Butler and Dunncliff, T., 1920, **117**, 649) that potassium hydrogen sulphate is unaffected when shaken with dry alcohol but that, when similarly treated, sodium hydrogen sulphate yields an intermediate sulphate having the composition $\text{Na}_3\text{H}(\text{SO}_4)_2$. Dry alcohol also reacts with ammonium hydrogen sulphate, yielding the corresponding sulphate, $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$ (Dunncliff, this vol., p. 476). Both these intermediate sulphates have been previously reported as phases in ternary systems, $\text{M}_2\text{SO}_4\text{--H}_2\text{SO}_4\text{--H}_2\text{O}$ ($\text{M} = \text{Na}$, Pascal and Ero, *Bull. Soc. chim.*, 1919, **39**, 1534; and $\text{M} = \text{NH}_4$, van Dorp, *Z. physikal. Chem.*, 1910, **73**, 284; see also D'Ans, *Z. anorg. Chem.*, 1913, **80**, 235).

Potassium hydrogen sulphate, trisodium hydrogen disulphate, and triammonium hydrogen disulphate all show a small fall in acidity when treated with dry alcohol. In the cases of the first two substances, this was ascribed to the presence of traces of water in the alcohol (T., 1920, **117**, 654). Further observations indicate that this view requires revision for the following reasons.

(1) Most carefully dried alcohol in which no test for water can be obtained acts on the three substances with a small but appreciable diminution of acidity. Hence, in order to free $\text{M}_3\text{H}(\text{SO}_4)_2$, obtained by the action of dry alcohol upon MHSO_4 , from acid, the product has to be washed with an inactive substance, ether, and not with alcohol.

(2) Dilute alcoholic sulphuric acids (less than 4 per cent.), produced by the action of alcohol (7 parts) on the hydrogen sulphates of potassium, sodium, or ammonium (1 part), do not appreciably reduce the acidity of a fresh quantity of potassium hydrogen sulphate, trisodium hydrogen disulphate, or triammonium hydrogen disulphate, respectively.

(3) Alcoholic sulphuric acids react with the normal sulphates of sodium and ammonium, giving a new solid phase. The nature of the chemical action depends on the temperature of the reaction and the concentration of the alcoholic sulphuric acid used.

(4) The solid phase produced by the action of alcohol on sodium hydrogen sulphate or ammonium hydrogen sulphate depends on the proportions of alcohol to hydrogen sulphate used.

These observed facts can all be explained if the hydrogen sulphates are regarded as composed of two components, M_2SO_4 and H_2SO_4 . When alcohol is added to one of these substances, a ternary system.

$M_2SO_4-H_2SO_4-C_2H_5O$, is developed. The possible solid phases are $M_2SO_4.H_2SO_4$; $xM_2SO_4.yH_2SO_4$; and M_2SO_4 . The systems in which $M = Na$ and NH_4 are under investigation by solubility measurements at atmospheric pressure and arbitrarily fixed temperatures. Results so far obtained indicate that, in the action of alcohol on compounds of the type $M_2SO_4.H_2SO_4$, acid is gradually and continuously removed from the solid phase, forming a second solid phase (or two entirely new solid phases) and a liquid phase (alcoholic sulphuric acid *) until a definite concentration of sulphuric acid in alcohol, in equilibrium with the two solid phases, is reached. In the univariant systems so developed four phases are assembled—two solid, one liquid, and one vapour.

Conversely, when alcoholic sulphuric acids * act on the normal or hydrogen sulphates of sodium or ammonium, action takes place with the formation of a new solid phase and a similar univariant system.

Hence the reduction of the acidity of potassium hydrogen sulphate, trisodium hydrogen disulphate, and triammonium hydrogen disulphate by the action of dry alcohol appears to be a normal reaction and not due to the presence of water as an impurity in the alcohol.

Attempts have been made to isolate other compounds of the type $M_2SO_4.H_2SO_4$ (Schultz, *Pogg. Ann.*, 1868, **133**, 137) in order to obtain a generalisation of the action of alcohol upon them.

Lithium Hydrogen Sulphate (van Dorp, *Z. physikal. Chem.*, 1910, **73**, 289).—Pure lithium sulphate (Found: $SO_4 = 87.50$. Calc., $SO_4 = 87.47$ per cent.) was made by igniting the monohydrate, purified by recrystallisation. Attempts to crystallise the hydrogen sulphate from aqueous solutions containing even a large excess of sulphuric acid yielded crystals of lithium sulphate monohydrate more or less contaminated with sulphuric acid, which was completely removed when the powdered crystals were extracted with ether. When lithium sulphate was dissolved by heating it with excess of sulphuric acid (d 1.6–1.7; Schultz, *loc. cit.*), crystals having the following composition separated on cooling: $H_2SO_4 = 38.71$; $Li_2SO_4 = 57.02$; $H_2O = 4.27$. Theory for $LiHSO_4$ requires $H_2SO_4 = 47.11$; $Li_2SO_4 = 52.89$ per cent. Of a series of samples, only one was obtained which gave an acidity (47.00 per cent.) corresponding with theory for lithium hydrogen sulphate. In all other preparations, the acidity was low. The acid is quantitatively extracted by alcohol or ether. A dry (ignited) porous saucer withdraws acid from the substance.

* The alcoholic sulphuric acids are always partly esterified, and this introduces a complication into the investigation.

Rubidium Hydrogen Sulphate.—Attempts to prepare rubidium hydrogen sulphate by treating rubidium nitrate with a small excess of sulphuric acid, evaporating to dryness, and igniting the residue were unsuccessful. This was due to the fact that it is difficult to remove the last traces of acidity from the preparation by prolonged ignition (compare Browning, *Z. anorg. Chem.*, 1902, 29, 140). The normal sulphate was made by evaporating a weighed quantity of rubidium nitrate with the calculated amount of sulphuric acid and igniting the residue (purity by SO_4 -estimation = 100.11 per cent.). An equivalent quantity of sulphuric acid was added to a weighed quantity of rubidium sulphate, dissolved in water. The solution was evaporated and the residue fused. The product was powdered in a hot agate mortar (acidity after extraction with ether = 26.95. Theory for RbHSO_4 requires 26.86 per cent.). It was not deliquescent. The compound was treated with seven times its weight of pure, dry alcohol and then extracted with ether. Acidity of residue = 26.93 per cent. Rubidium hydrogen sulphate was also prepared from rubidium chloride and gave similar results. Rubidium hydrogen sulphate is not appreciably acted upon by either alcohol or ether.

Cæsium hydrogen sulphate was prepared from the nitrate by a method exactly similar to that described for the rubidium salt. Purity by SO_4 -estimation = 100.20 per cent. The salt contained a trace of potassium. It was not deliquescent. Acidity of ether-extracted CsHSO_4 = 21.55 per cent. (theory for CsHSO_4 requires 21.32 per cent.). After treatment with seven times its weight of alcohol for eighteen hours and subsequent washing with ether, its acidity was 21.36 per cent. Hence, cæsium hydrogen sulphate is not appreciably attacked by either alcohol or ether.

Preparations of the hydrogen sulphates of silver, strontium, and barium were attempted. Silver sulphate was dissolved in excess of hot concentrated sulphuric acid and the crystals which separated on cooling were drained in a desiccator. They were then pressed on a dried porous saucer. The barium and strontium salts were prepared by the same method, but the product was separated by centrifugalisation. Both compounds were crystalline.

Silver Hydrogen Sulphate.—Fine crystals, which turned blue on exposure to light (Found: H_2SO_4 = 25.20. Calc. for AgHSO_4 , H_2SO_4 = 24.55 per cent.). After the compound had been kept for forty-eight hours on a porous saucer, the acidity fell to 12.08 per cent. Ether or alcohol extracts all the acid and, in the process, a large quantity of ethyl hydrogen sulphate is formed. When no attempt is made to protect from light the substance undergoing extraction, the residue is black.

Barium Hydrogen Sulphate.—Original acidity = 46.40 per cent. $\text{BaSO}_4 \cdot 2\text{H}_2\text{SO}_4$ requires 45.94 per cent. $\text{BaSO}_4 \cdot \text{H}_2\text{SO}_4$ requires 29.60 per cent. of H_2SO_4 . After the compound had been kept on a porous saucer, the following acidities were recorded at intervals: 30.00; 19.80; 14.61; 12.41 and 8.99 per cent. Ether or alcohol extracts all the acid from these compounds. The rapidity of extraction is increased by pounding up the substance at intervals.

Strontium Hydrogen Sulphate.—Acidity after isolation and pressure on a porous saucer = 34.24 per cent. ($\text{SrSO}_4 \cdot \text{H}_2\text{SO}_4$ requires 26.59 per cent.). Acidities determined on successive days = 24.09; 15.93; 13.67 per cent. Alcohol or ether gradually extracts all the acid from the substance.

The hydrogen sulphates may be classified under four headings according to their behaviour with alcohol and ether.

(1) *Converted into neutral sulphate by alcohol or ether.*

Lithium hydrogen sulphate. Also the hydrogen sulphates of silver, strontium, and barium.

(2) *Converted into $\text{M}_2\text{H}(\text{SO}_4)_2$ by alcohol (5–7 parts). Unaffected by ether.*

Sodium hydrogen sulphate; ammonium hydrogen sulphate.

(3) *Slightly affected by alcohol (7 parts). Unaffected by ether.*

Potassium hydrogen sulphate; tri-sodium hydrogen disulphate; triammonium hydrogen disulphate.

(4) *Not appreciably affected by alcohol or ether.*

Rubidium hydrogen sulphate; caesium hydrogen sulphate.

The amount of decomposition of the hydrogen sulphates of the alkali metals by alcohol decreases with increase in atomic weight of the metal.

The hydrogen sulphates in classes (1) and (2) are deliquescent. Those in classes (3) and (4) are not deliquescent. Those hydrogen sulphates which are deliquescent are also considerably or completely decomposed by alcohol.

Deliquescence.—If sodium hydrogen sulphate is dissolved in water, the first solid phase to separate on evaporation is the normal sulphate. An attempt was made to determine the composition of the first solid phase obtained when very small quantities of water act on sodium hydrogen sulphate. This was done by allowing sodium hydrogen sulphate, exposed in thin layers, to deliquesce. The action was stopped arbitrarily. The "deliquesced" substance was first extracted with ether in a Soxhlet apparatus to remove water and free sulphuric acid. Ether does not react with the sulphates of sodium. The acidity of the solid phase was then determined, and the weight of residue on ignition (to discover if any water was present). The solid was next treated with dry alcohol

and washed with ether, and the acidity of the resultant compound determined. The analysis depends on the condition that alcohol will decompose sodium hydrogen sulphate, giving trisodium hydrogen disulphate, whilst the latter salt already present will be negligibly affected. The results are given below. The temperature was 30° and the vapour pressure 31.51 mm.

Deliquescence of Sodium Hydrogen Sulphate.

	i.	ii.	iii.
Water absorbed, calculated as percentage of the sodium hydrogen sulphate used	5.10	6.92	12.42
Percentage acidity after ether-extraction of the substance after deliquescence	33.36	31.10	28.18
Percentage acidity of the residue after treatment with alcohol and washing with ether	18.50	18.47	18.51

Theory for $\text{Na}_2\text{H}(\text{SO}_4)_2$ requires 18.71 per cent. of H_2SO_4 .

These figures may indicate that, under these conditions at the time the deliquescence was stopped, the solid phases were sodium hydrogen sulphate (unchanged) and trisodium hydrogen disulphate, and the liquid phase, sulphuric acid and water, with a very small concentration of sodium sulphate. Similar results were obtained for ammonium hydrogen sulphate on incomplete deliquescence.

The Reaction between the Fused Hydrogen Sulphate of Sodium and of Ammonium and the Normal Sulphates of the Alkali Metals and of Ammonium.

The action of alcohol on a mixture of molecular proportions of sodium sulphate and sodium hydrogen sulphate corresponds with the removal of sulphuric acid and the formation of trisodium hydrogen disulphate from the sodium hydrogen sulphate present. If the mixture be heated above the temperature of fusion and below the temperature of decomposition of sodium hydrogen sulphate, a product will be obtained which is sparingly attacked by alcohol and shows that there has been considerable formation of the compound having the formula $\text{Na}_2\text{H}(\text{SO}_4)_2$. Now if fused sodium hydrogen sulphate combines directly with sodium sulphate, one would hope also to obtain evidence of the direct formation of an analogous "mixed" intermediate sulphate, for example, $\text{NaR}_2\text{H}(\text{SO}_4)_2$, stable to alcohol, when the normal sulphate of a different alkali metal, R, is heated with fused sodium hydrogen sulphate.

If, on the other hand, sodium hydrogen sulphate be regarded as composed of two components, Na_2SO_4 and H_2SO_4 , the examination of the reaction which takes place when it is fused in contact with the normal sulphate of a different element, R, will involve the investigation of the ternary system $\text{R}_2\text{SO}_4\text{-Na}_2\text{SO}_4\text{-H}_2\text{SO}_4$. In the

instance quoted above, there would be a two-component system, and the compound $\text{Na}_3\text{H}(\text{SO}_4)_2$ or $3\text{Na}_2\text{SO}_4 \cdot \text{H}_2\text{SO}_4$ would be formed by the establishment of equilibrium of the sulphuric acid between the sodium sulphate presented as such and the sodium sulphate originally present as $\text{Na}_2\text{SO}_4 \cdot \text{H}_2\text{SO}_4$. (A similar argument applies to the corresponding ammonium salts.)

By examination of the results of fusion of MHSO_4 ($\text{M} = \text{Na}$ or NH_4) with R_2SO_4 ($\text{R} = \text{Li}, \text{NH}_4, \text{Na}, \text{K}, \text{Rb}, \text{or Cs}$), the author hoped to obtain some insight into the reaction which takes place.

The following assumptions, based on experimental evidence, are made :

(1) MHSO_4 is decomposed by alcohol, giving $\text{M}_3\text{H}(\text{SO}_4)_2$.

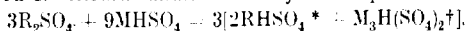
(2) Fused MHSO_4 can part with sulphuric acid under suitable conditions (*vide* Note I, p. 738).

(3) $\text{M}_3\text{H}(\text{SO}_4)_2$; KHSO_4 ; RbHSO_4 ; CsHSO_4 are not appreciably affected by treatment with dilute alcoholic sulphuric acids, produced on treatment of the melt containing excess of MHSO_4 with alcohol.

The action is confined to the hydrogen sulphates of sodium and ammonium because (1) they have low melting points, (2) they are the only two hydrogen sulphates obtainable in a state of purity which have also been shown to give a definite product on treatment with seven times their weight of alcohol, and (3) the method of analysis is not applicable to compounds theoretically producible from the hydrogen sulphates of potassium, rubidium, and caesium.

The reaction may proceed according to four types, a comparison of which is facilitated by using the simplest formulæ and taking 9 moles of MHSO_4 to 3 of R_2SO_4 . In practice, excess of MHSO_4 over these proportions was taken. The nature of the reaction was determined by comparison of the experimental with the calculated values for each type and by determination of the composition of the solid phase after alcohol treatment.

TYPE I.—*Alcohol extracts no acid from the powdered melt.*

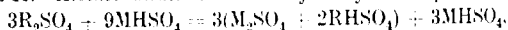


after alcohol treatment $\rightarrow 3[2\text{RHSO}_4 + \text{M}_3\text{H}(\text{SO}_4)_2]$.

If $\text{R} = \text{Na}$ or NH_4 , alcohol removes $2\text{H}_2\text{SO}_4$ from the melt.

If $\text{R} = \text{Li}$, alcohol removes $3\text{H}_2\text{SO}_4$ from the melt.

TYPE II.—*Alcohol extracts 1 molecule of acid from the powdered melt.*

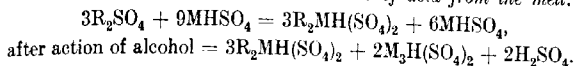


after alcohol treatment $\rightarrow 3(\text{M}_2\text{SO}_4 + 2\text{RHSO}_4) + \text{M}_3\text{H}(\text{SO}_4)_2 + \text{H}_2\text{SO}_4$.

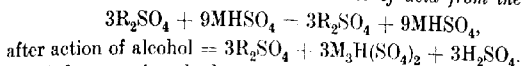
With excess of MHSO_4 , this could not be realised. A secondary action would take place between M_2SO_4 and MHSO_4 (*vide* Note I).

* The general case would give $x\text{R}_2\text{SO}_4 \cdot y\text{H}_2\text{SO}_4$. † *Vide* Note I.

TYPE III.—*Alcohol extracts 2 molecules of acid from the melt.*



TYPE IV.—*Alcohol extracts 3 molecules of acid from the melt.*



Dried ammonium hydrogen sulphate of slightly low acidity was treated as a mixture of NH_4HSO_4 and $(NH_4)_3H(SO_4)_2$ (this vol., p. 478) and the results were calculated accordingly.

As an example of the procedure, the action of ammonium hydrogen sulphate (more than 3 mols.) on rubidium sulphate (1 mol.) will be taken. A mixture of the two substances in known proportions was heated in a platinum basin at 190° for five minutes. After the ammonium hydrogen sulphate had fused, the basin was removed and the solidified melt (the loss of weight was negligible) was powdered in a hot agate mortar and replaced in the platinum basin. It was twice again melted and pulverised and then its acidity determined. It was treated with seven times its weight of dry alcohol for eighteen hours, and the product washed with ether and its acidity determined. This was checked against theory as calculated on the weights of the substances taken. A complete analysis of the product was often made. The acidities calculated for the four types were: Type I, 22.77, Type II, 19.78, Type III, 16.57, Type IV, 13.08 per cent. Experimental value = 22.87 per cent. Therefore the type of reaction is No. 1 and the products of reaction $RbHSO_4$ and $(NH_4)_3H(SO_4)_2$. Several preparations were made of each kind in which the proportions of $MHSO_4$ to R_2SO_4 varied. A typical example is given under each head. Ether has no action on the powdered melts.

(1) $Li_2SO_4 + NaHSO_4$. Residual acidity = 15.39 per cent. Theory for Type IV = 15.65 per cent. There is no action between lithium sulphate and sodium hydrogen sulphate.

(2) $(NH_4)_2SO_4 + NaHSO_4$. Results valueless. Ammonium sulphate decomposes below the melting point of sodium hydrogen sulphate.

(3) $Na_2SO_4 + NaHSO_4$. Residual acidity = 18.62 per cent. Product of reaction, $Na_3H(SO_4)_2$. *Vide* Note I.

(4) $K_2SO_4 + NaHSO_4$. Residual acidity = 23.15 per cent. Theory for Type I = 24.90 per cent. Results low for potassium hydrogen sulphate (Type I), but very high for other types. Calculated composition of the product of reaction, $4K_2SO_4 \cdot 3H_2SO_4$ together with $Na_3H(SO_4)_2$ (Type I).

(5) $Rb_2SO_4 + NaHSO_4$. Residual acidity = 20.84 per cent.

Theory for Type I = 20.55 per cent. Products of reaction, RbHSO_4 and $\text{Na}_3\text{H}(\text{SO}_4)_2$.

(6) $\text{Cs}_2\text{SO}_4 + \text{NaHSO}_4$. Residual acidity = 20.29 per cent. Theory for Type I = 19.92 per cent. Products of reaction, CsHSO_4 and $\text{Na}_3\text{H}(\text{SO}_4)_2$.

(7) $\text{Li}_2\text{SO}_4 + \text{NH}_4\text{HSO}_4$. Residual acidity = 16.70 per cent. Theory for Type IV = 16.72 per cent. There is no action.

(8) $(\text{NH}_4)_2\text{SO}_4 + \text{NH}_4\text{HSO}_4$. Residual acidity = 19.68 per cent. Theory for Type I or III = 19.84 per cent. Product of reaction, $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$. *Vide* Note I.

(9) $\text{Na}_2\text{SO}_4 + \text{NH}_4\text{HSO}_4$. Residual acidity = 19.26 per cent. Theory for Type I = 19.46 per cent.; theory for Type III = 19.52 per cent. *Vide* Note II.

(10) $\text{K}_2\text{SO}_4 + \text{NH}_4\text{HSO}_4$. Residual acidity = 21.21 per cent. Theory for Type I = 25.69 per cent.; theory for Type III = 18.69 per cent. Calculated composition (Type I) approx. $2\text{K}_2\text{SO}_4 \cdot \text{H}_2\text{SO}_4$ and $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$.

(11) $\text{Rb}_2\text{SO}_4 + \text{NH}_4\text{HSO}_4$. Residual acidity = 22.87 per cent. Theory for Type I = 22.77 per cent. Products of reaction, RbHSO_4 and $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$.

(12) $\text{Cs}_2\text{SO}_4 + \text{NH}_4\text{HSO}_4$. Residual acidity = 20.87 per cent. Theory for Type I = 20.57 per cent. Products of reaction, CsHSO_4 and $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$.

NOTE I.—The interaction of the hydrogen sulphates of sodium and ammonium with the normal sulphates with the formation of either unmixed intermediate sulphates or hydrogen sulphates ($x\text{R}_2\text{SO}_4 \cdot y\text{H}_2\text{SO}_4$) is in conformity with the representation of the hydrogen sulphates as composed of two components, M_2SO_4 and H_2SO_4 , and with the view that the reactions observed involve the transfer of sulphuric acid from the hydrogen sulphate to the normal sulphate in the establishment of equilibrium. The hydrogen sulphate (in excess) is converted into a compound or mixture, $a\text{M}_2\text{SO}_4 \cdot b\text{H}_2\text{SO}_4$, which, with alcohol, gives the intermediate sulphate, $\text{M}_3\text{H}(\text{SO}_4)_2$. Hence, it appears that Nos. (2) and (8) are of Type I and not of Type III.

NOTE II.—This would suggest that the final products in No. (9) are $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$ and $\text{Na}_3\text{H}(\text{SO}_4)_2$ and that the reaction does not give any mixed intermediate sulphate (Type III).

NOTE III.—There is no evidence of the formation of a "mixed" intermediate sulphate (Type III) in any of the reactions.

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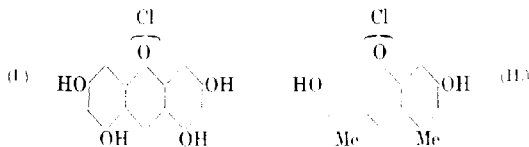
LAHORE, PUNJAB, INDIA.

[Received, November 16th, 1922.]

LXXXVII.—*A Direct Synthesis of certain Xanthylum Derivatives.*

By DAVID DOIG PRATT and ROBERT ROBINSON.

IN the course of experiments on the synthesis of pyrylium salts related to the anthocyanidins attempts have been made to condense together under the influence of hydrogen chloride at the ordinary temperature a reactive phenol, a carboxylic acid or a derivative thereof, and a fatty-aromatic ketone. Particularly when the phenol employed was phloroglucinol the formation of oxonium compounds was frequently observed, but further investigation showed that the ketone added did not participate in the reaction and that the products were xanthylum salts. A short digression from the main course of the investigation has been made in order to study this reaction and to determine the conditions most favourable for its occurrence. Apparently the only acid which gives satisfactory results is formic acid, and this may be applied in the form of ester or ortho-ester. The various phenols behave very differently and fall into five groups represented by phloroglucinol, orcinol, β -naphthol, resorcinol, and *m*-cresol. When hydrogen chloride is passed into a cold solution of phloroglucinol in ethyl formate, orange crystals of 1:3:6:8-tetrahydroxyxanthylum chloride (I) will begin to separate in two or three minutes and the yield ultimately obtained is almost quantitative. The experiment represents what is probably the simplest recorded formation of an oxonium salt containing the pyrylium nucleus and is admirably suited for purposes of demonstration. Under similar conditions, orcinol behaves in an analogous manner, but the reaction is sluggish. In this case a satisfactory yield of 3:6-dihydroxy-1:8-dimethylxanthylum chloride (II) is best obtained by leading hydrogen chloride through a solution of the dihydric phenol in a mixture of ethyl formate and ethyl orthoformate.



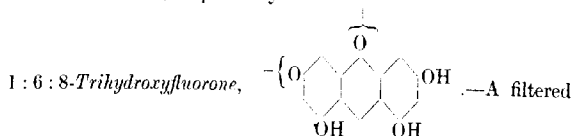
β -Naphthol requires ethyl orthoformate alone, and the yield of dinaphthapyrylium chloride is not good. The method provides a convenient process for the rapid preparation of this salt in small quantities. In presence of hydrogen chloride, resorcinol (and

pyrogallol) condenses slowly with ethyl formate and rapidly with a mixture of ethyl formate and ethyl orthoformate, but the product is abnormal and has not yet been completely investigated. It is undoubtedly an oxonium salt and dissolves in water, the colour of the solution resembling that of the permanganates. Addition of sodium acetate precipitates an orange-yellow compound. Only traces of oxonium salts were obtained from most phenols, for example, from quinol, catechol, phenol, and *m*-cresol. Obviously the reaction is of limited application, but it gives very good results in the two cases first mentioned, and it is unlikely that these examples are unique.

EXPERIMENTAL.

1:3:6:8-Tetrahydroxyxanthylum Chloride (Formula I).—A moderate stream of hydrogen chloride was passed through a cold solution of anhydrous phloroglucinol (5 grams) in ethyl formate (30 c.c.) during twenty minutes. The liquid at once assumed a clear orange colour and crystallisation of the product commenced in two minutes. An equal volume of ether was added and the substance then collected, washed with ether, and dried in the air: 5.7 grams of an orange-yellow powder were obtained. On warming with water, an orange-brown solution was produced and there was also a small, flocculent precipitate. The addition of a drop of hydrochloric acid gave a clear yellow solution, from which the chloride crystallised in microscopic, yellow, rectangular prisms. These did not redissolve on heating and were very sparingly soluble in hot dilute hydrochloric acid. In more concentrated acid, they dissolved readily, and this behaviour probably indicates that a dihydrochloride was formed. The salt was crystallised from hot, very dilute hydrochloric acid and dried in a vacuum (Found: C = 52.5; H = 3.9. $C_{13}H_9O_5Cl \cdot H_2O$ requires C = 52.4; H = 3.7 per cent.). On heating, the salt darkens at 100° , probably owing to loss of solvent of crystallisation: it then becomes dark brown at 250° , but does not melt or suffer serious decomposition below 330° . The substance is insoluble in most organic solvents, but dissolves readily in methyl or ethyl alcohol to an orange solution. The solution in alkalis is orange-red. The *sulphate* is a sparingly soluble salt, obtained as an orange-red, flocculent precipitate, becoming crystalline on boiling, when water is at once added to a solution of the chloride in concentrated sulphuric acid. The *picrate* crystallises from dilute solutions in hot ethyl alcohol in yellow needles. From more concentrated solutions a red modification separates in addition. The yellow needles darken, but do not melt when heated at 330° . The ferrichloride having the normal composition could not be

obtained. The derivative prepared in the usual manner was crystallised from acetic acid. The slender, yellow needles darkened at 280°, became almost black at 310°, but did not melt at 330° (Found: C = 57.3; H = 3.6 per cent.). Another specimen was crystallised from ethyl alcohol containing ferric chloride and hydrochloric acid. The microscopic, yellow prisms became black at about 300°, but did not melt (Found: C = 51.2; H = 3.9 per cent.). Both specimens appeared to be homogeneous and contained iron, and are probably double compounds of the ferrichloride with the acetate and chloride, respectively.

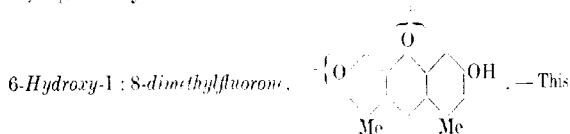


solution of potassium acetate in ethyl alcohol was added to a hot filtered solution of tetrahydroxyxanthylum chloride in the same solvent. An orange-red precipitate was at once thrown down and this was collected, washed with water, and dried at 150°. The substance then assumed a deep red colour; it darkened slightly, but did not melt at 330° (Found: C = 64.1; H = 3.3. $C_{13}H_8O_5$ requires C = 63.9; H = 3.3 per cent.). The substance is very sparingly soluble in most organic solvents, but dissolves in alcohol to a yellow solution exhibiting green fluorescence. It is moderately soluble in hot water, and the red solution becomes yellow on the addition of a drop of hydrochloric acid: subsequently tetrahydroxyxanthylum chloride will crystallise out in the usual form. The formula employed at the head of this section, and also below, to represent the constitution of a fluorone requires some explanation. Essentially it expresses the phenol-betaine view of the nature of these substances and is in accordance with Pfeiffer's theory of betaines (*Ber.*, 1922, 55, [B], 1762). The conception that the molecule has a bipolar salt-like character is in harmony with the physical and chemical properties of the fluorones, but the subject need not be discussed in detail in this place, because experimental work is in progress which has a direct bearing on the problem.

3 : 6-Dihydroxy-1 : 8-dimethylxanthylum Chloride (Formula II).—Oreinol (5 grams) was dissolved in ethyl formate (20 c.c.) and ethyl orthoformate (5 c.c.), and a slow stream of hydrogen chloride passed through the solution during three-quarters of an hour. The liquid became red very quickly and after about five minutes crystallisation of the product could be induced by cooling and scratching the sides of the containing vessel. After allowing to remain during about twelve hours, the separated crystals, which filled the liquid,

were collected, washed with ether, and dried in the air (4.7 grams). The crude product, an orange-brown powder, is pure enough to be utilised in most experiments and is difficult to recrystallise owing to its extremely sparing solubility. From a large volume of very dilute boiling hydrochloric acid it separates in red prisms exhibiting a striking green glance (Found: C = 61.2; H = 5.3. $C_{15}H_{13}O_5Cl \cdot H_2O$ requires C = 61.2; H = 5.1 per cent.). This salt blackens at about 280° , but does not melt below 330° . It is readily soluble in methyl or ethyl alcohol to red solutions, but is very sparingly soluble or insoluble in other organic solvents. Unlike the phloroglucinol derivative just described, it does not appear to form a dichloride and does not dissolve in moderately concentrated hydrochloric acid. When the chloride is washed repeatedly on a filter with hot dilute sodium acetate solution, it is converted into the fluorone described below.

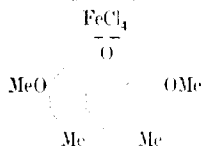
The chocolate powder was washed with water, dried, and dissolved as far as possible in boiling glacial acetic acid. On cooling, the filtered red solution deposited needles which in mass are reddish-brown and exhibit a fine green reflex, whilst under the microscope the individual, transparent crystals are seen to be orange-yellow. The substance was collected and dried in a vacuum over sulphuric acid (Found: C = 64.4; H = 5.6. $C_{17}H_{16}O_5 \cdot H_2O$ requires C = 64.2; H = 5.7 per cent.). This substance is therefore the acetate with one molecule of water of crystallisation. On heating, it darkens at 290° and appears to melt at 305° . *Dihydroxydimethylanthylum picrate* separates in glistening, golden-yellow leaflets when aqueous picric acid is added to a solution of the chloride in dilute hydrochloric acid. The derivative, which may be crystallised from alcohol, darkens at 230° and decomposes at 252° . The ferrichloride is probably abnormal, like the corresponding phloroglucinol derivative. It crystallises from acetic acid in yellowish-brown prisms with intense peacock-blue reflex. When heated at 330° , it gradually blackens but does not melt.



substance is probably identical with the "homofluorescein" obtained by Schwarz (*Ber.*, 1880, **13**, 543) by the action of chloroform and potassium hydroxide on orcinol, and also with the hydroxy-dimethylfluorone which Möhlau and Koch (*Ber.*, 1894, **27**, 2890) prepared by the action of aluminium chloride on methylenediorcinol. It is most conveniently obtained by the action of hot aqueous sodium

acetate on dihydroxydimethylxanthylum chloride. The crude product was washed with water, dried, and crystallised from glacial acetic acid containing sodium acetate. As stated above, the substance is sparingly soluble in hot glacial acetic acid and crystallises as an acetate, but it is much more soluble in presence of sodium acetate and separates on cooling as free fluorone. The compound has a great tendency to retain mineral matter, and the earlier specimens prepared gave, on analysis, results which were about 5 per cent. too low in carbon. Using pure materials and washing the crystals thoroughly with hot water, a pure product was obtained, and this was dried at 150° (Found: C = 74.9; H = 5.1. $C_{15}H_{12}O_3$ requires C = 75.0; H = 5.0 per cent.). The fluorone crystallises in dark red needles which exhibit a green reflex, and on heating it darkens at 280°, but does not melt at 330°. It is very sparingly soluble in organic solvents, but dissolves to some extent in boiling ethyl or isoamyl alcohol and crystallises on cooling the solutions. It is also slightly soluble in hot water to a yellow solution. Although extremely sparingly soluble in cold water, it imparts a vivid green fluorescence to the solution. The smallest visible crystal smeared on filter-paper and added to 100 c.c. of water produces a remarkably brilliant effect, which only reaches its full intensity after some hours owing to the slowness of the process of solution. The fluorescence in alcoholic solution is greenish-yellow.

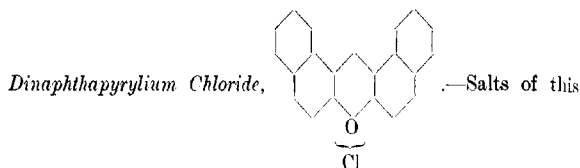
3 : 6-Dimethoxy-1 : 8-dimethylxanthylum Ferrichloride,



—Dihydroxydimethylxanthylum chloride (2.5 grams), suspended in ethyl alcohol (100 c.c.), was gradually treated with a large excess of methyl sulphate (50 c.c.) while concentrated aqueous sodium hydroxide was added from time to time so as to keep the solution alkaline. The reaction product was diluted with water and a yellow precipitate separated. This was converted into a *ferrichloride* by the addition of an excess of ferric chloride dissolved in concentrated hydrochloric acid, and the derivative was collected and crystallised from acetic acid (yield = 3.0 grams). The substance was recrystallised from acetic acid, in which it is somewhat sparingly soluble, and obtained in orange-yellow, lanceolate crystals melting at 221° after darkening at 200° (Found: C = 44.0; H = 2.9. $C_{15}H_{12}O_3Cl_3Fe$ requires C = 43.8; H = 3.8 per cent.).

The substance dissolves in sulphuric acid to a yellow solution

exhibiting green fluorescence, and in hot water to a yellow solution which gives a straw-coloured precipitate on the addition of sodium acetate.



series are readily accessible and have been more thoroughly investigated than any other oxonium compounds. The long series of papers by Fosse from 1901 onwards have brought to light many surprising reactions of the related pseudo-base, and a complete list of references will be found in Meyer and Jacobson's "Lehrbuch," 1920, Vol. II, Part III, 771. The substances described below have been previously obtained by Fosse, but we contribute some new details in regard to them. β -Naphthol (10 grams) is dissolved in ethyl orthoformate (15 c.c.), and a slow stream of hydrogen chloride passed through the cold solution during three hours. The liquid quickly darkens and crystallisation may be induced after thirty minutes. After allowing to remain in a closed vessel during twelve hours, the dinaphthapyrylium chloride is precipitated by the addition of ether, and then collected, washed with ether, and dried (2.0 grams). The main product of the reaction is β -naphthyl ethyl ether, and this could be isolated from the filtrate. The crude salt is practically pure and on boiling with water gives a slightly pink precipitate of bis(dinaphthapyryl) ether, which after crystallisation melts at 250° . *Dinaphthapyrylium picrate* separates in glistening needles when a solution of picric acid in acetic acid is added to a solution of dinaphthapyrylium chloride in the same solvent. This beautiful substance is reddish-crimson and has a coppery lustre. It melts at 239° , having lost its metallic appearance at 205° . *Dinaphthapyrylium ferrichloride* is extremely sparingly soluble in boiling acetic and formic acids, and can best be prepared in a crystalline condition by mixing hot dilute solutions of dinaphthapyrylium chloride and ferric chloride in glacial acetic acid. It separates in glistening, orange-brown needles melting at 288° (Found: C = 52.9; H = 2.9. $C_{21}H_{13}OCl_4Fe$ requires C = 52.7; H = 2.7 per cent.).

The use of derivatives of acids other than formic acid was not found to give satisfactory results in syntheses of xanthylum salts. When hydrogen chloride was passed into a solution of phloroglucinol in ethyl acetate, an intense yellow colour was developed and

a small amount of a yellow oxonium salt separated. This was collected and found to crystallise from dilute hydrochloric acid in bright yellow balls of needles, and in its reactions it closely resembled tetrahydroxyxanthylum chloride, of which it is doubtless the 9-methyl derivative. The main product was an uncrystallisable viscid oil.

One of us (D.D.P.) desires to express his gratitude to the Carnegie Trust for the award of a Scholarship which has enabled him to take part in this investigation.

CHEMISTRY RESEARCH LABORATORY,

THE UNITED COLLEGE OF ST. SALVATOR AND ST. LEONARD,

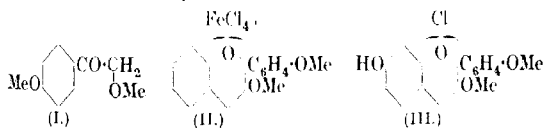
THE UNIVERSITY, ST. ANDREWS. [Received, March 7th, 1923.]

LXXXVIII.—*A Synthesis of Pyrylium Salts of Anthocyanidin Type. Part II.*

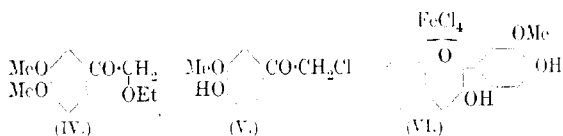
By DAVID DOIG PRATT and ROBERT ROBINSON.

IN Part I (T., 1922, **121**, 1580), a preliminary account was given of a method of preparation of certain derivatives of 3-hydroxy-pyrylium, which is the characteristic nucleus of the anthocyanidin salts derived by hydrolysis of the naturally occurring anthocyanin pigments. Some further examples of the application of the process are now recorded. The methoxy-compounds related to the ethoxy- and phenoxy-derivatives described in the earlier communication have been prepared from *ω*-methoxyacetophenone. Magnesium anisyl bromide and methoxyacetonitrile yield, ultimately, *ω*:4-dimethoxyacetophenone (I), and this ketone is readily converted into pyrylium salts which are more intensely coloured than those derived from *ω*-methoxyacetophenone. By condensation with salicylaldehyde in alkaline solution and treatment of the resulting unsaturated ketone with hydrogen chloride in ether, the oxonium salt was produced in good yield; the substance was analysed in the form of its *ferrichloride* (II), which crystallises in red needles.

ω:4-Dimethoxyacetophenone and resorcyaldehyde condense in glacial acetic acid solution under the influence of hydrogen chloride with formation of 7-hydroxy-3:4'-dimethoxy-2-phenylbenzopyrylium chloride (III), which crystallises in crimson needles.

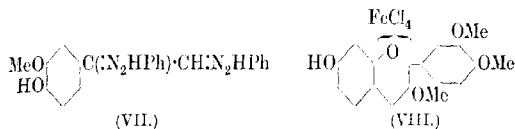


The introduction of further hydroxyl or alkyloxy-groups into the acetophenone component in these syntheses was found to be a matter of considerable difficulty. Whereas, as is well known, *p*-bromoanisole reacts readily enough with magnesium with formation of a normal organo-magnesium derivative, 4-bromoveratrole could not be converted into magnesium veratryl bromide. The interaction of methoxyacetoneitrile and catechol or veratrole in the presence of a variety of catalysts yielded only traces of the desired products. The condensation of ethoxyacetyl chloride and veratrole under the influence of aluminium chloride in carbon disulphide solution led to the formation of a substance which should be *o*-ethoxyacetoveratrone (IV), since it gives the expected analytical results. But this substance cannot be employed for the preparation of pyrylium salts, since it condenses neither with salicylaldehyde in alcoholic solution containing potassium hydroxide nor with resorcyaldehyde under the usual conditions. There is certainly some dubiety in regard to the constitution of this compound, but it is difficult to suggest an alternative view of its nature. Better results in this series were obtained in the following manner. A good yield of *o*-chloroacetovanillone (V) results from the condensation of chloroacetyl chloride and veratrole in cold carbon disulphide solution in presence of aluminium chloride. The constitution of the substance follows from its reduction to acetovanillone, which can be effected by treatment with iron and sulphuric acid in alcoholic solution. The reaction has been previously studied under more drastic conditions which involve complete demethylation of the product (Stephen and Weizmann, T., 1914, 105, 1048). The ferrichloride (VI) was obtained from the chloro-ketone by succes-



sive treatment with potassium acetate in boiling alcoholic solution, salicylaldehyde in alcoholic potassium hydroxide, hydrogen chloride and hydroferrichloric acid. The first stage is no doubt the production of *o*-acetoxyacetovanillone, and this may be hydrolysed by boiling with an aqueous suspension of barium carbonate to *o*-hydroxyacetovanillone, which has been characterised by its dehydrodiphenylhydrazone (VII). By methylation of *o*-chloroacetovanillone, the known *o*-chloroacetoveratrone was obtained and this was hydrolysed to *o*-hydroxyacetoveratrone by a method similar to that already mentioned. The uncrystallisable oil was

then methylated by means of silver oxide and methyl iodide, and the crude *o*-methoxyacetoveratrone condensed with resorcyaldehyde in the usual way. The salt was isolated as ferrichloride (VIII) and is of interest because on demethylation it should yield the anthocyanidin corresponding to the flavonol fisetin (IX). In order to render

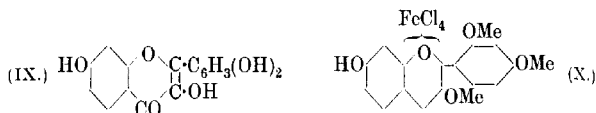


an extended examination of this interesting compound a feasible proposition, we are attempting to devise an improved method of preparation of *o*-methoxyacetoveratrone. The specimen of the latter substance which we have employed distilled over a small range of temperature, but as it could not be crystallised we consider that it must contain some impurity. The oil could be completely converted into two quite distinct semicarbazones, both of the expected formula, $C_{12}H_{17}O_4N_3$. One of these is undoubtedly the semicarbazone of *o*-methoxyacetoveratrone, and the other may be a stereoisomeric semicarbazone of the same ketone. In view, however, of the possible conversion of the *o*-hydroxyacetoveratrone into a related α -hydroxyveratrylacetaldehyde in the faintly alkaline aqueous solution, a change analogous to that of fructose into glucose, it is also conceivable that the second semicarbazone has the formula $(MeO)_2C_6H_3·CH(OMe)·CH·N·NH·CO·NH_2$.

The point will be decided subsequently if we are fortunate enough to succeed in preparing *o*-methoxyacetoveratrone by a process not depending on methylation of veratrylcarbinol, and in the meantime the semicarbazones are designated as veratrylmethoxyacetaldehyde semicarbazones (*a*) and (*b*). We had hoped that it would be possible to recover the pure ketone from the semicarbazone, but this does not appear to be practicable, as hydrolysis under all conditions attempted leads to decomposition. As we design to prepare ultimately the anthocyanidin corresponding to morin, *o*-hydroxyresacetophenone derivatives have been investigated from the point of view of their applicability to the synthesis of pyrylium salts.

o:2:4-Trimethoxyacetophenone (Slater and Stephen, T., 1920, 117, 314) and resorcyaldehyde yield the salt (X), but in this case a considerable amount of a dark crimson by-product is formed. A similar substance is the sole product of the condensation of resorcyaldehyde and *o*-methoxyresacetophenone (Slater and Stephen, *loc. cit.*, p. 312) in glacial acetic acid solution by means of

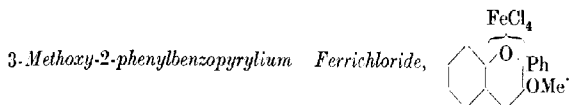
hydrogen chloride. This substance is crystalline and produced in high yield, but its investigation is not yet completed.



Comparison of 2-phenylbenzopyrylium salts with corresponding substances containing a hydroxyl or an alkyloxy-group in position 3 shows that the latter are the more intensely coloured. The formation of colourless pseudo-bases under the appropriate conditions first observed by Willstätter and his collaborators with the natural pigments, is characteristic of the 3-oxy-substituted pyrylium types. This statement applies to salts of true flavylium structure, hydroxylated in the positions 7 or 4' so that the formation of a quinhydrone or quinonoid anhydro-colour-base is a possibility. Within these limits of comparison, the favourable influence of the attachment of oxygen to position 3 on ease of pseudo-base formation is very noticeable.

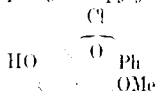
EXPERIMENTAL.

ω-Methoxyacetophenone, $C_6H_5 \cdot CO \cdot CH_2 \cdot OMe$.—This ketone has been obtained by a method which is essentially that adopted by Sommelet for the preparation of *ω*-ethoxyacetophenone (*Ann. Chim.*, 1906, **9**, 521). An ethereal solution of methoxyacetoneitrile (10.4 grams; Polstorff and Meyer, *Ber.*, 1912, **45**, 1911) was gradually added with cooling to a solution of magnesium phenyl bromide (from 22.9 grams of bromobenzene and 3.5 grams of magnesium in 150 c.c. of ether). The colourless additive compound separated at once and, after allowing to remain during twelve hours, the mixture was decomposed by ice-cold water and then by means of cold dilute sulphuric acid. The separated ethereal layer was washed with aqueous sodium carbonate and water and dried by anhydrous sodium sulphate. After removal of the solvent, the residual oil was distilled under reduced pressure. *ω*-Methoxyacetophenone is a colourless, mobile oil which boils at 228–230°/760 mm. and 118–120°/15 mm. (Found: C = 72.2; H = 6.6. $C_9H_{10}O_2$ requires C = 72.0; H = 6.7 per cent.) (n_D^{20} = 1.5416 by the Abbé instrument). The substance is readily soluble in most organic solvents and condenses with 6-aminopiperonal, on warming in methyl-alcoholic solution containing a little potassium hydroxide, to a *methoxymethylenedioxyphenylquinoline* which exhibits a fine violet fluorescence in dilute acetic acid solution. The *semicarbazone* crystallises from ethyl alcohol in small, colourless needles melting at 85°.



—The condensation of ω -methoxyacetophenone and salicylaldehyde was effected exactly as already described in Part I (*loc. cit.*, p. 1580) in the case of ω -ethoxyacetophenone. Four grams of ω -methoxyacetophenone yielded 3.5 grams of pure phenyl 2-hydroxy-3-methoxystyryl ketone, $\text{HO}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{C}(\text{Bz})\cdot\text{OMe}$, which crystallises from methyl alcohol in almost colourless, rectangular prisms melting at 155° . The substance is rather sparingly soluble in alcohol and ether and dissolves in dilute alkali to an orange-yellow solution. This unsaturated ketone (5 grams), dissolved in anhydrous ether (100 c.c.), was converted into the oxonium ferrichloride by the successive action of hydrogen chloride and ferric chloride dissolved in concentrated hydrochloric acid as recorded in the case of the ethoxy-analogue (*loc. cit.*), the yield being 5 grams. The substance crystallises very well from acetic acid in long, golden-yellow, rectangular prisms melting at 118° (Found: C = 44.5; H = 3.1. $\text{C}_{16}\text{H}_{13}\text{O}_2\text{Cl}_4\text{Fe}$ requires C = 44.3; H = 3.0 per cent.). This salt is sparingly soluble in chloroform to an orange-yellow solution and dissolves readily in methyl alcohol to a yellow solution which, on the addition of water, gives at first a colourless suspension and then on warming a clear, colourless solution which soon becomes faintly yellow. Addition of hydrochloric acid regenerates the oxonium salt. The ferrichloride is decomposed by water, and the pseudobase passes into the colourless solution. The yellow solution in concentrated sulphuric acid exhibits pale ivy-green fluorescence.

7-Hydroxy-3-methoxy-2-phenylbenzopyrylium Chloride,



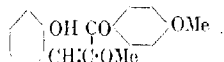
—When a stream of hydrogen chloride was passed through a solution of ω -methoxyacetophenone (4.5 grams) and 3-resorecyaldehyde (4.1 grams) in glacial acetic acid (10 c.c.), orange-red crystals of the oxonium salt soon began to separate and, after allowing to remain during a few hours, completely filled the liquid. The substance was collected, washed with ether, and dried (7.0 grams). A further quantity can be recovered from the filtrate by the addition of ether or in the form of ferrichloride. The substance was crystallised from hot dilute hydrochloric acid and obtained in clusters of orange-red needles which, after drying in a vacuum over sulphuric acid, were found to be anhydrous (Found: C = 66.7; H = 4.7.

$C_{16}H_{13}O_3Cl$ requires C = 66.6; H = 4.5 per cent.). On heating, the salt darkens at 190° and decomposes at 202° . It is soluble in alcohol and chloroform to yellow and orange-red solutions, respectively. The yellow solution in concentrated sulphuric acid exhibits bright apple-green fluorescence. A carmine precipitate of the colour base is produced by the addition of sodium acetate to a moderately concentrated solution in dilute hydrochloric acid and when the substance is so obtained it shows no tendency to change. If, however, an excess of tap-water is added to a little of the finely pulverised chloride, a clear, bright carmine solution is obtained and this rapidly becomes colourless on the addition of a drop of acetic acid, whilst hydrochloric acid regenerates the yellow colour of the oxonium salt. With distilled water, the reaction is different, a pale yellow solution being produced at once, and this is decolorised in a few seconds, the orange-yellow colour being restored by the addition of hydrochloric acid. If a drop of neutral calcium chloride solution is added to the distilled water, the reaction resembles that of tap-water. On warming with sodium acetate or on treatment with sodium carbonate or sodium hydroxide in the cold, all forms, oxonium salt, pseudo-base, and colour-base, give yellow solutions which no doubt contain the corresponding unsaturated ketone. The *ferrichloride* crystallises from acetic acid in red, hexagonal prisms which exhibit a green lustre and melt at 143° after softening at 134° . At the suggestion of Dr. R. C. Menzies we have examined the *double thallic chloride*, which is obtained as a red precipitate when a hydrochloric acid solution of thallic chloride is added to a solution of the oxonium chloride. The substance crystallises from acetic acid in brick-red needles melting at 144° . The analytical results indicate a complex composition, but reference to the literature shows that this is the rule rather than the exception among thallic compounds (Found: C = 46.0, 45.9; H = 4.8, 4.4; loss at 100° = 5.7. $3C_{16}H_{13}O_3Cl \cdot 2FeCl_3 \cdot 4H_2O$ requires C = 46.1; H = 3.9; H_2O = 5.8 per cent.). The substance, dried at 100° , lost no further weight at 120° .

ω -4-Dimethoxyacetophenone (Formula I).—This ketone was prepared from magnesium anisyl bromide and methoxyacetonitrile by the method described above in the case of *o*-methoxyacetophenone. The yield from 20 grams of the nitrile was 15 grams of the pure substance boiling at $185-190^\circ/35$ mm. The colourless oil crystallised on cooling and rubbing and the compound was recrystallised by the addition of much light petroleum to a moderately concentrated solution in benzene. The colourless, glistening plates melt at 46° (Found: C = 66.8; H = 6.5. $C_{10}H_{12}O_3$ requires C = 66.7; H = 6.7 per cent.).

ω :4-Dimethoxyacetophenone is readily soluble in organic solvents with the exception of light petroleum. The *dimethoxymethyl-enediaryphenylquinoline* obtained by condensation with 6-aminopiperonal exhibits bright, pure blue fluorescence in dilute acetic acid solution. The *semicarbazone* crystallises from alcohol in colourless plates melting at 149°.

4-Methoxyphenyl 2-Hydroxy-5-methoxystyryl Ketone,



—A mixture of ω :4-dimethoxyacetophenone (4 grams), salicylaldehyde (2·8 grams), potassium hydroxide (1·5 grams), and methyl alcohol (100 c.c.) was boiled under reflux during two hours, cooled, diluted with water, and acidified by acetic acid. The crude product so precipitated was collected (3·0 grams) and crystallised from methyl alcohol, in which, as in ethyl alcohol and ether, the substance is somewhat sparingly soluble. It crystallises in small, almost colourless, rectangular prisms melting at 160° (Found: C = 71·9; H = 5·8. $\text{C}_{17}\text{H}_{14}\text{O}_4$ requires C = 71·8; H = 5·6 per cent.). The compound dissolves readily in chloroform and in dilute aqueous potassium hydroxide to an orange-yellow solution.

3:4'-Dimethoxy-2-phenylbenzopyrylium Ferrichloride (Formula II).—The unsaturated ketone described in the preceding section (3·0 grams), dissolved in dry ether (100 c.c.), was converted into the pyrylum salt by the action of a stream of hydrogen chloride during an hour. After the addition of a solution of ferric chloride in hydrochloric acid, the solvent was removed by careful distillation and the precipitate of ferrichloride collected and dried (2·8 grams). The substance crystallises very well from glacial acetic acid, being readily soluble in the hot solvent and sparingly soluble in the cold, and separates in clusters of hair-fine, orange-red needles melting at 135° (Found: C = 44·0; H = 3·1. $\text{C}_{17}\text{H}_{15}\text{O}_3\text{Cl}_4\text{Fe}$ requires C = 44·0; H = 3·2 per cent.). This salt dissolves in alcohol and chloroform to yellow and red solutions, respectively. The orange-red solution in dilute hydrochloric acid becomes colourless on the addition of sodium acetate and the colour is restored by reacidification. The vivid jade-green fluorescence which is exhibited by a solution in concentrated sulphuric acid is much bluer and brighter than that given by 3-methoxy-2-phenylbenzopyrylium ferrichloride (see above).

7-Hydroxy-3:4'-dimethoxy-2-phenylbenzopyrylium Chloride (Formula III).—Hydrogen chloride was passed during one and a half hours through a solution of ω :4-dimethoxyacetophenone (5·0 grams) and β -resoreylaldehyde (4·1 grams) in glacial acetic acid (10 c.c.).

The liquid quickly assumed a violet-red colour and after about twenty minutes crystallisation of the product commenced. The chloride was collected, washed with ether, and dried (7.0 grams). This salt crystallised from hot dilute hydrochloric acid in intense crimson, very slender needles, which were dried over sulphuric acid in a vacuum (Found: C = 60.8; H = 5.0. $C_{17}H_{15}O_4Cl \cdot H_2O$ requires C = 60.7; H = 5.1 per cent.). The substance decomposes at 218° after darkening from 206° . It dissolves in chloroform to an orange-red solution and in alcohol to a yellow solution. The fluorescence of a solution in concentrated sulphuric acid is brilliant apple-green. The colour-base is obtained as a dark reddish-violet precipitate on the addition of sodium acetate to a solution of the chloride in dilute hydrochloric acid. The finely ground salt, treated with an excess of tap-water, gives a fine intense bluish-red solution which, if very dilute, is decolorised on standing during about half an hour and rapidly on the addition of a trace of acetic acid. The yellow colour of the oxonium salt is restored by the addition of hydrochloric acid. The chloride gives with a large excess of distilled water a yellow solution containing some pseudo-base, that is, the colour is intensified by acidification; the addition of a few c.c. of tap-water causes complete decoloration. Evidently pseudo-base formation depends in this case on the hydrogen-ion concentration of the solution, the limits between which this may vary being very close together. The oxonium chloride, the colour-base, or the pseudo-base gives with dilute aqueous sodium hydroxide an orange-yellow solution containing the unsaturated ketone in which the pyran ring is broken. On acidification, a colourless solution is obtained and this becomes yellow on heating owing to the formation of the oxonium salt. A similar scission of the ring does not appear to result in this example when cold aqueous sodium carbonate is employed instead of the hydroxide. The *ferrichloride*, prepared in the usual manner, crystallises from acetic acid in deep red, elongated, rectangular prisms melting at 162° . Its solution in alcohol is orange-red and in chloroform pink.

ω-Ethoxyaceto-veratrone (Formula IV).—Powdered, freshly prepared, anhydrous aluminium chloride (11.5 grams) was added to a mixture of veratrole (11.5 grams) and carbon disulphide (50 c.c.). Ethoxyacetyl chloride* (10 grams) was then gradually introduced

* Ethoxyacetyl chloride was prepared by the method of Henry (*Ber.*, 1869, 2, 276), but the following slight modification very materially increases the yield. Phosphorus trichloride (20 grams) was slowly added in the cold to pure ethoxyacetic acid (40 grams) and the reaction was completed by gentle heating on the steam-bath until the evolution of hydrogen chloride ceased. The mixture was cooled and the chloride poured away from the phosphorous acid and distilled. The yield was 42 grams of material boiling at 127° .

and when the reaction had subsided a further quantity of aluminium chloride (11.5 grams) was added in small portions at one time. After decanting the carbon disulphide from the dark, viscous mass, the product was decomposed by ice water and dilute hydrochloric acid and distilled in steam in order to remove any unchanged veratrole. The residual oil was taken up in ether, and the ethereal solution washed with dilute aqueous sodium hydroxide, dried with calcium chloride, and evaporated. On distillation of the residue, 8.0 grams of an oil boiling at $245\text{--}250^\circ/20\text{ mm.}$ were obtained. The substance solidified on cooling and was crystallised from a mixture of benzene and light petroleum. The colourless prisms melted at 68° (Found: $C = 64.1$; $H = 7.2$. $C_{12}H_{16}O_4$ requires $C = 64.3$; $H = 7.1$ per cent.). This ketone, if it is a ketone, does not appear to yield a semicarbazone, nor does it condense with salicylaldehyde in methyl alcoholic solution containing potassium hydroxide. With resorcydaldehyde in glacial acetic acid solution in presence of hydrogen chloride, it yields a crimson condensation product, which is not a pyrylium salt, but is soluble in ether. The crimson colour is destroyed by water and a solid colourless compound is produced. Similar results were obtained with veratrole itself. Presumably these compounds are triphenylmethane derivatives.

ω -Chloroacetovanillone (Formula V).—The preparation of this substance followed exactly the details of that described above for the supposed ethoxyacetoveratrone. The quantities used were: veratrole, 40 grams; chloroacetyl chloride, 34 grams; carbon disulphide, 150 c.c.; aluminium chloride, two portions of 40 grams each. The ethereal solution was not washed with sodium hydroxide, but was dried and evaporated, when, on cooling, the residue solidified completely and weighed 42 grams. The substance was crystallised from alcohol and then from benzene and obtained in colourless prisms melting at 102° (Found: $C = 53.7$; $H = 4.6$. $C_9H_9O_3Cl$ requires $C = 53.8$; $H = 4.4$ per cent.). The melting point is the same as that of ω -chloroacetoveratrone, but the new compound is completely soluble in dilute aqueous potassium hydroxide and gives a green colour on the addition of ferric chloride to its alcoholic solution. The following experiment was carried out in order to determine the position of the methoxy-group.

Reduction to Acetovanillone.—The chloro-ketone (5 grams), dissolved in aqueous alcohol, was reduced at 60° by means of dilute sulphuric acid (5 c.c. of 10 per cent.) and iron filings (3 grams). The mixture was mechanically stirred during three hours and the product isolated by extraction with ether. After removing the solvent from the dried solution, the pale yellow oil which remained solidified, and was found to be free from chlorine. On crystal-

lisation from benzene, colourless prisms melting at 115° were obtained. These gave a green coloration in alcoholic solution and a blackish-violet in aqueous solution on the addition of ferric chloride. The formation of dehydrodiacetovanillone was also observed. Finally the phenylhydrazone was prepared and this melted at 125° after crystallisation. These properties are identical with those of acetovanillone as described by Neitzel (*Ber.*, 1891, **24**, 2863) and quite different from those of *iso*acetovanillone, m. p. 91° (Schneider and Kraft, *Ber.*, 1922, **55**, [B], 1892). It may be mentioned that acetovanillone can be readily converted into a salicylidene derivative, and this yields a pyrylium salt on heating with concentrated hydrochloric acid. The addition of sodium acetate to an aqueous solution causes the separation of a bluish-red colour-base, and the reaction is diagnostic of the free hydroxyl group in the para-position in the benzene nucleus.

4-Hydroxy-3-methoxyphenylglyoxal diphenylhydrazone (Formula VII) and *3:4'-Dihydroxy-3'-methoxy-2-phenylbenzopyrylium Ferrichloride* (Formula VI).—An alcoholic solution of ω -chloroacetovanillone (24 grams) and potassium acetate (20 grams) was boiled under reflux during two hours. The alcohol was then removed by distillation and the oil, precipitated by the addition of water, taken up in ether. The ethereal solution was washed, dried, and evaporated, and the residual oil (15 grams) (A), which could not be crystallised, was hydrolysed by boiling water (500 c.c.) and barium carbonate (8 grams) during two hours. The product, which doubtless consisted of ω -hydroxyacetovanillone, could also not be crystallised, but on warming with a dilute acetic acid solution of phenylhydrazine it furnished a copious precipitate of an osazone-like derivative. The substance was collected, dried, and crystallised from glacial acetic acid. It separated in short, yellow needles melting at 186° (Found: C = 70.2; H = 5.4; N = 15.3. $C_{21}H_{20}O_2N_4$ requires C = 70.0; H = 5.5; N = 15.5 per cent.). The compound is sparingly soluble in organic solvents to yellow solutions and in sulphuric acid to a greenish-brown solution. In attempting the condensation of ω -hydroxyacetovanillone with salicylaldehyde in alkaline solution, there was no point in carrying out the second stage of hydrolysis described above. The crude acetoxyacetovanillone (A) (5 grams) was mixed with salicylaldehyde (2.5 grams), potassium hydroxide (2.0 grams), and methyl alcohol (100 c.c.), and the whole boiled under reflux during one hour. The diluted and cooled liquid was acidified with acetic acid, and the condensation product, which separated as a pale yellow, heavy oil, was separated by decantation of the supernatant liquid, washed with water, and dried. The substance was dissolved in ether (100 c.c.), and a current of hydrogen

chloride passed through the solution during an hour. Dilute hydrochloric acid was then added, the ether removed by distillation, and a ferrichloride precipitated by the addition of a concentrated solution of ferric chloride in hydrochloric acid. The dark brown, viscous mass (1.0 gram) was dissolved in a very little hot glacial acetic acid and on cooling deposited clusters of red needles which were collected, washed, and dried in a vacuum over sulphuric acid (Found: C = 41.3; H = 2.8. $C_{16}H_{13}O_4Cl_4Fe$ requires C = 41.1; H = 2.7 per cent.). This substance melts at 142° and is much more soluble in acetic acid than any of the other ferrichlorides described in this paper. It is soluble in chloroform and alcohol to rose solutions and in the latter case the colour fades. The solution in sulphuric acid exhibits weak olive-green fluorescence. In a large excess of tap-water, it gives a violet solution, from which the colour-base gradually separates, leaving a colourless solution. The latter contains the pseudo-base and on the addition of sodium carbonate or hydrochloric acid gives a yellow coloration for the different reasons which have been explained in other cases. The orange-red solution of the salt in very dilute hydrochloric acid yields the violet colour-base on the addition of sodium acetate, but decoloration is rapid in dilute solution. Sodium carbonate added to an alcoholic solution produces a dull violet coloration, and this is of some interest because Willstätter has used this reaction as one indication of the position of methyl groups in ethers of cyanidin and delphinidin. Probably a blue coloration with sodium carbonate in alcoholic solution will only denote a free hydroxyl group in the pyrylium nucleus when the number and position of the hydroxyl groups in the aromatic nuclei are comparable with those of one of the natural pigments.

o-Methoxyacetoveratrone. $MeO \cdot C_6H_2 \cdot CO \cdot C_6H_3(OMe)_2$.—A solution of 4-bromoveratrole in dry ether gradually dissolved activated magnesium on boiling, but very little organo-magnesium derivative was produced. The breakdown of this route induced us to test the applicability of the Hoesch reaction to catechol derivatives, but the results were not encouraging. Methoxyacetoneitrile could not be condensed with catechol by means of hydrogen chloride in ethyl or *iso*amyl ethereal solution in the presence or absence of zinc chloride and at the ordinary temperature or the boiling points of the solvents. Methoxyacetoneitrile and veratrole in carbon disulphide solution under the influence of aluminium chloride gave a small yield of a substance, possibly methoxyacetoveratrone, but the reactions of the compound were ambiguous. Carbomethoxyglycollonitrile* appears

* The following method of preparation of this substance is much more convenient and gives a better yield than that recommended by Sonn and

to condense to some extent with catechol in ethereal solution in presence of hydrogen chloride, but as the product did not yield a pyrylium salt by condensation with resorcyaldehyde it was not further investigated. The desired substance has, however, been obtained by the following series of processes. ω -Chloroacetovanillone was converted into ω -chloroaceto-veratrone by the method which Stephen and Weizmann (*loc. cit.*) employed for the methylation of ω -chloroacetocatechone. ω -Chloroaceto-veratrone (24 grams) was treated for two hours with a boiling alcoholic solution of potassium acetate (20 grams). The acetoxy-derivative was isolated by extraction with ether, and the uncrystallisable oil (15 grams) was then further hydrolysed by boiling during two hours with water (500 c.c.) containing precipitated barium carbonate (8 grams) in suspension. The ω -hydroxyaceto-veratrone was also isolated by repeated extraction with ether and was an uncrystallisable syrup (7 grams). This substance was characterised by its *dehydrodiphenylhydratone*, which crystallises from acetic acid in microscopic, yellow, rectangular prisms melting at 164° . A solution of hydroxyaceto-veratrone reduces Fehling's solution even in the cold.

ω -Hydroxyaceto-veratrone (10 grams), thoroughly dried, was dissolved in methyl iodide (28 grams), and after the addition of silver oxide (25 grams) the mixture was boiled under reflux during six hours. The product was dissolved in ether and the solution filtered and distilled. 3.4 Grams of an oil boiling at $200-205^{\circ}/25$ mm. were obtained, but all efforts to induce the crystallisation of the compound were unsuccessful. The result of condensation with resorcyaldehyde, described in the next section, shows that this substance is essentially methoxyaceto-veratrone. In the hope of obtaining a characteristic derivative from which the pure ketone could be regenerated, the semicarbazone was prepared. This was easily produced in the usual manner in aqueous solution in presence of a little methyl alcohol, but on crystallisation from methyl alcohol two substances

Falkenheim (*Ber.*, 1922, **55**, [B], 2975). Methyl chloroformate (21.7 grams) was gradually added with cooling and shaking to a mixture of aqueous formaldehyde (20 c.c. of 35 per cent.) and potassium cyanide (15 grams), dissolved in water (45 c.c.). The agitation was continued during one and a half hours by mechanical means and the oil was then extracted with ether, the ethereal solution separated, washed, and dried with sodium sulphate. After removing the solvent, the residual oil was distilled and the yield of the nitrile, b. p. $96-97^{\circ}/12$ mm., was 15.0 grams. ω -Carbomethoxyfisetol (Somn and Falkenheim, *loc. cit.*) is obtainable in excellent yield by the condensation of carbomethoxyglycollonitrile and resorcinol in ethereal solution by means of hydrogen chloride, followed by hydrolysis of the ketimine salt. The use of zinc chloride is quite unnecessary, and this has already been shown to be the case in connexion with the preparation of ω -methoxyresacetophenone by Slater and Stephen (*loc. cit.*).

were separated. The possible nature of these is discussed on p. 747. *Veratrylmethoxyacetaldehydesemicarbazone-a* is much the more sparingly soluble and crystallises in prisms melting at 205° (Found: C = 54.1; H = 6.6. $C_{12}H_{11}O_4N_3$ requires C = 53.9; H = 6.4 per cent.). *Veratrylmethoxyacetaldehydesemicarbazone-b* crystallises in woolly needles melting at 168° (Found: C = 54.1; H = 6.5 per cent.). Attempts to hydrolyse these semicarbazones by hydrochloric acid, alone or in presence of formaldehyde or benzaldehyde, resulted in decomposition of the nitrogen-free product.

7-Hydroxy-3:3':4'-trimethoxy-2-phenylbenzopyrylium Ferri-chloride (Formula VIII).—A stream of hydrogen chloride was passed during an hour and a half through a mixture of crude ω -methoxyacetoveratrone (0.5 gram), β -resorcyaldehyde (0.3 gram), and acetic acid (1 c.c.), when the pyrylium chloride separated in dark violet crystals with a beetle-green lustre. The substance could be crystallised from dilute hydrochloric acid in brown prisms, which, crystallising in a film on a glass surface, appear to be purple by transmitted light. The ferrichloride was prepared by adding the whole product to hot dilute hydrochloric acid and treating the filtered solution with ferric chloride and hydrochloric acid. The derivative crystallised from acetic acid in red needles melting at 156° (Found: C = 41.9; H = 3.5. $C_{18}H_{17}O_5Cl_2Fe$ requires C = 42.2; H = 3.3 per cent.). The salt dissolves in alcohol to an orange-red solution and in chloroform to a pink solution. The fluorescence in sulphuric acid is not very marked and is a weak olive-green. The colour-base is thrown down by the addition of sodium acetate to a solution in dilute hydrochloric acid and is a purple precipitate. A bright purple solution is obtained when an excess of tap-water is added to a little of the ferrichloride. This soon fades to pink and is ultimately decolorised. The process is hastened by the addition of a trace of acetic acid.

7-Hydroxy-3:2':4'-trimethoxy-2-phenylbenzopyrylium Ferri-chloride (Formula X).— ω -Methoxyresacetophenone and ω -carbo-methoxyfisetol (Sonn and Falkenheim, *loc. cit.*) yield abnormal products on condensation with β -resorcyaldehyde, and the investigation of these substances is not yet complete. ω :2:4-Tri-methoxyacetophenone (2 grams) and an equal weight of β -resorcyaldehyde, dissolved in acetic acid (15 c.c.), were condensed together by the agency of a stream of hydrogen chloride during two hours. A small amount of crystals separated from the dark bluish-red solution, but the whole was added to boiling dilute hydrochloric acid (500 c.c.), and the deep orange solution filtered from a dark reddish-violet by-product. The pyrylium chloride separated on cooling as a flocculent, red precipitate. The ferrichloride was prepared in the

usual manner and crystallised from acetic acid in beautiful golden-brown clusters of lanceolate needles which had a striking green glance. The substance melts at 160° without obvious decomposition (Found: C = 42.0; H = 3.5. $C_{18}H_{17}O_5Cl_4Fe$ requires C = 42.2; H = 3.3 per cent.). The reactions of this substance closely resemble those of the isomeride described in the preceding section. The slow evaporation of the red solution in chloroform produced some large crystals which had a particularly brilliant beetle-green lustre. The green fluorescence of the solution in concentrated sulphuric acid was a little brighter than that of the related catechol derivative.

It is hoped to include in a subsequent communication some account of the position of the absorption bands in the visible region of the spectrum which are characteristic of the oxonium salts and colour-bases now described.

One of us (D. D. P.) desires to express his thanks to the Carnegie Trust for a scholarship which has enabled him to take part in this investigation.

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LXXXIX.—*Physostigmine. Part I. Alkylation Products of Eseroline.*

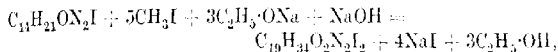
By GEORGE BARGER and EDGAR STEDMAN.

THE partial synthesis of physostigmine (eserine) from methylcarbimide and eseroline by Polonovski and Nitzberg (*Bull. Soc. chim.*, 1916, [iv], 19, 27) has reduced the problem of the constitution of this alkaloid to that of elucidating the structure of eseroline. With this end in view, one of us (E. S., T., 1921, 119, 891) attempted to prepare the methyl ether of eseroline methiodide, $C_{14}H_{21}ON_2I$, by acting on it with methyl iodide and sodium ethoxide, in ethyl-alcoholic solution. A new sparingly soluble methiodide was obtained, to which the formula $C_{10}H_{17}ON_2I$ was assigned at the time, and this new salt was accordingly regarded as a degradation product of eseroline; the "inexplicable nett loss of C_4H_4 " could not, however, be accounted for.

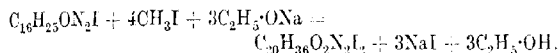
We soon found that the first stage of the reaction consists (as was to be expected) in the methylation of the phenolic hydroxyl which in physostigmine is united to the grouping $NHMeCO$.

The new salt gives off one methyl group when boiled with hydriodic acid, and is not more soluble in sodium hydroxide than in water. We therefore started with an ether of eseroline, choosing the ethyl ether eserethole, which is conveniently prepared by Polonovski's method (*Bull. Soc. chim.*, 1915, [iv], 17, 240) and can be readily purified by distillation. The use of this ether has the further advantage of obviating the necessity of carrying out the reaction in a hydrogen atmosphere. From eserethole methiodide, and also from the corresponding ethiodide, we obtained analogous quaternary salts, but their analysis and that of their derivatives finally convinced us, however, that instead of being simpler than eseroline, they are in reality more complex. The formula of the original compound, $C_{10}H_{17}ON_2I$, has to be approximately doubled, to $C_{19}H_{34}O_2N_2I_2$. The recognition of the correct formula was much delayed by faulty nitrogen analyses according to Dumas; nitric oxide was discovered in the nitrogen evolved, and its formation could never be entirely suppressed, but good analyses were subsequently obtained by the micro-Kjeldahl method.

The reaction, first described, must therefore be formulated in some such way as this:



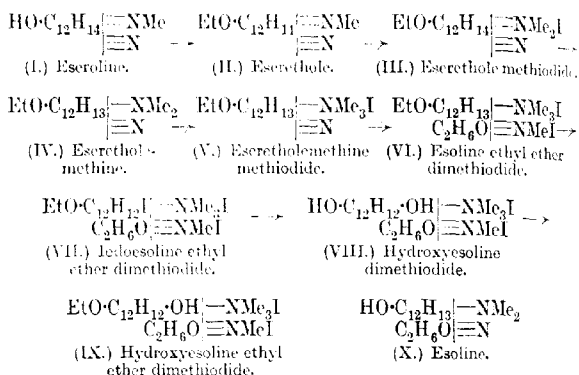
and that with eserethole methiodide as



These reactions are therefore extensive methylations. In spite of the fact that eserethole methiodide appears to be fully methylated, it takes up four further carbon atoms in the presence of sodium ethoxide and methyl iodide. Straus (*Annalen*, 1913, 401, 350) had indeed already indicated that eseroline has a slight tendency to take up two molecules of methyl iodide, but the introduction of a larger number of methyl groups had not been observed at all. Straus (*loc. cit.* and *Annalen*, 1914, 406, 332) has suggested a formula for eseroline which represents it as consisting of a benzene and a piperidine ring, joined by a pyrrole ring. According to the subsequent nomenclature of Perkin and Robinson, it might be termed a hydroxydi-N-methylhexahydronorharmen, and physostigmine would thus show analogies to harmine and harmaline. We have been tempted to employ Straus's eseroline formula to explain the formation of the compounds described in the present paper, but as the formula is open to certain objections, it is perhaps preferable to limit ourselves at present to partly developed formulae, and to suggest merely in general terms that the reaction under discussion

might consist in an opening of a piperidine ring, a methylation of the methine thus formed, and a methylation of the pyrrole ring with the production of an indoline derivative with methyl groups in position 2. It is only in this way that the introduction of so many methyl groups can be explained.

In order to facilitate nomenclature, we suggest the name "esoline" for a phenolic ditertiary base, $C_{16}H_{26}O_2N_2$ (X). The salt first described two years ago is then the dimethiodide of esoline methyl ether, and the salts from eserethole are diquaternary salts of esoline ethyl ether (VI), etc. The chief reactions carried out, together with the hypothetical base esoline, may be represented as follows:



Eseretholemethine (IV) was first prepared by Max and Michel Polonovski (*Bull. Soc. chim.*, 1918, [iv], 23, 337) by the action of cold sodium hydroxide on eserethole methiodide and they also prepared its methiodide (V). We find that if this salt is heated with methyl iodide and sodium ethoxide in ethyl alcoholic solution, the same diquaternary salt (VI) is formed as from eserethole methiodide itself, so that the methiodide of the methine is undoubtedly an intermediate product in the reaction under discussion. The subsequent stages consist in the addition of methyl iodide to the second nitrogen atom and in the addition of the elements of a molecule of ethyl alcohol. We consider that in the formation of eseretholemethine a methylene group is left attached (in position 2) to the pyrrole ring and that it is here that C_2H_6O is fixed by the double bond, but whether as hydroxyl + ethyl, or hydroxyl + 2 methyls, or as an ether, we cannot at present say quite definitely. An ether grouping in this position is, however, very improbable, for by boiling quaternary salts of esoline ethyl ether with hydriodic

acid, only one alkyl group (the ethyl of eserethole) is eliminated, and the resulting phenolic salts are found to contain only two carbon atoms less than the original. We have considered the possible occurrence of an ether grouping in this position mainly because Perkin and Robinson (T., 1919, 115, 946) found two methoxy-groups in the base, obtained by the action of methyl alcoholic potassium hydroxide on the normal methosulphate of methyltetrahydroharmine (compare also O. Fischer, *Ber.*, 1914, 47, 104). The extent of the analogies and differences between methyltetrahydroharmine and eseroline methyl ether requires further study; however, it should be remembered at the outset that the latter substance contains two more hydrogen atoms than the former.

In the above partly developed formulae we have made as few assumptions as possible, and have not assigned a methyl group to the second, non-basic nitrogen atom of eserethole. Straus (*Annalen*, 1914, 406, 336) found two *N*-methyl groups in eseroline, in contradiction to earlier investigators, who had found only one. The second methyl group is, according to him, only given off when a relatively very large quantity of hydriodic acid is employed (in Pregl's micro-apparatus) and may well be of a different nature from the first *N*-methyl group. The doubt is increased by the fact that Polonovski and Nitzberg subsequently (*Bull. Soc. chim.*, 1916, [iv], 19, 27) found that eseroline reacts with phenylcarbimide to form a substituted carbamide, which seems to imply the existence of an imino-group in the molecule.

The second nitrogen atom of eseroline is not wholly devoid of basic properties, since Straus (*Annalen*, 1913, 401, 361) found that physostigmine forms in concentrated hydrochloric acid a dichloroaurate and that eseroline methiodide may in part loosely combine with a second molecule of methyl iodide. During the action of methyl iodide and sodium ethoxide on eserethole, the basic character of the second nitrogen is so much enhanced that ultimately a stable diquaternary iodide results.

We have attempted the degradation of eseroline ether dimethiodides in various ways. Potassium permanganate, whether before or after the removal of the *O*-alkyl group, did not give any satisfactory results. Boiling 33 per cent. nitric acid left the salts intact, but at 150° gave a crystalline oxidation product which was not further investigated. Short boiling with nitric acid (*d* 1.4) liberates iodine and forms a diquaternary nitrate containing a single atom of iodine, which with potassium iodide furnishes a sparingly soluble iodo-dimethiodide (VII). Similar iodinations with iodine and nitric acid have been observed by Mrs. Robinson (T., 1916, 109, 1079). In

the present case, the new iodine atom does not appear to be in a benzene ring, for boiling hydriodic acid replaces it by hydroxyl; at the same time the ethoxy-group is hydrolysed, with formation of (VIII). This substance on re-ethylation only takes up one ethyl group, in the original hydroxyl of eserethole. The new hydroxyl is not attacked.

Results which will probably be of great use have been obtained by the decomposition of esoline ethyl ether diquaternary hydroxide, which appears to furnish a ditertiary base (esoline ethyl ether *i*), and a monotertiary base formed from the latter by the further loss of trimethylamine and water. We hope soon to give an account of these bases, and to discuss the conclusions to be drawn from our identification of eserethole methiodide, m. p. 171° , of Max and Michel Polonovski with the "hydroiodide," m. p. 170° , of the methine (*Bull. Soc. chim.*, 1918, [iv], **23**, 337, 338). This identity may be connected with observations by Brunner on alkylene indolines (*Ber.*, 1905, **38**, 1359) and by Decker on other bases (compare, for example, *Ber.*, 1905, **38**, 2493).

There are two further points to which we wish to direct attention. The esoline salts are optically inactive, and the optical activity was lost after the eseretholemethine stage. Whether esoline contains no asymmetric carbon atom, or whether its metho-salts are racemic, we cannot as yet say; we have not yet attempted their resolution.

Physostigmol ethyl ether, formed by heating eserethole methiodide, gives, even in very dilute solution, a blue coloration with dimethylaminobenzaldehyde and hydrochloric acid, confirming Straus's view that physostigmol is an indole derivative. None of the substances described in the present paper gives even a trace of this colour reaction. It is evident that the formation of physostigmol is accompanied by a rather deep-seated change: a dihydro-indole becomes an indole, and the substituent in either the 2 or the 3 position is removed. Apart from the elucidation of the constitution of physostigmol, the chief problem is to determine the *mechanism* of its formation.

EXPERIMENTAL.

Esoline Methyl Ether Dimethiodide, ($C_{19}H_{34}O_2N_2I_2$).—This compound, to which the incorrect formula $C_{10}H_{17}ON_2I$ was previously assigned, is prepared by the method described in a previous paper (*loc. cit.*). It contains one methoxyl group (Found: MeO = 5.12. $C_{19}H_{34}O_2N_2I_2$ requires 1MeO = 5.38 per cent.). When this result is combined with an estimation of *O*-methyl + *N*-methyl groups by Herzig and Meyer's method, the presence of either four or five *N*-methyl groups is indicated [Found: Me(O- + N-) =

14.04. Calc., $6\text{Me}(\text{O} + \text{N}) = 15.6$; $5\text{Me}(\text{O} + \text{N}) = 13.0$ per cent. Found: C = 39.08; H = 5.51; N (micro-Kjeldahl) = 4.80 per cent. $\text{C}_{19}\text{H}_{34}\text{O}_2\text{N}_2\text{I}_2$ requires C = 39.58; H = 5.90; N = 4.86 per cent.].

Esoline Methyl Ether Dimethoperchlorate, $\text{C}_{19}\text{H}_{34}\text{O}_2\text{N}_2(\text{ClO}_4)_2$.—When an aqueous solution of the diquaternary hydroxide obtained from methylesoline dimethiodide by treatment with silver oxide is mixed with a solution of perchloric acid, a precipitate of the *dimethoperchlorate* is formed. This salt is sparingly soluble in water or alcohol and can be crystallised from either of these solvents or, more conveniently, from a mixture of the two. It forms prisms which melt at 294° . It decomposes violently when heated on a platinum foil [Found: Cl = 13.33.* $\text{C}_{19}\text{H}_{34}\text{O}_2\text{N}_2(\text{ClO}_4)_2$ requires Cl = 13.63 per cent.].

Esoline Ethyl Ether Dimethiodide, $\text{C}_{20}\text{H}_{36}\text{O}_2\text{N}_2\text{I}_2$.—The preparation of this compound was first undertaken with a view to ascertaining if methylation of the hydroxy-group in eseroline was the first stage in the formation of methylesoline dimethiodide. The method employed was similar to that used in the case of the latter compound, except that the displacement of air by hydrogen was unnecessary. One gram of eserethole methiodide was dissolved in 5 c.c. of a solution of 0.5 gram of sodium in 25 c.c. of ethyl alcohol, excess of methyl iodide was then added, and the mixture heated under reflux on a water-bath for three and a half hours. (The reaction apparently proceeds more slowly than in the case of the lower homologue; the first separation of solid occurred only after the mixture had been heated for two hours.) The mixture was then cooled and filtered (yield 0.35 gram). When recrystallised from methyl alcohol, *esoline ethyl ether dimethiodide* forms short prisms which melt at about 208° with decomposition (Found: C = 41.22; H lost; N (micro-Kjeldahl) = 4.51; I = 43.29. $\text{C}_{20}\text{H}_{36}\text{O}_2\text{N}_2\text{I}_2$ requires C = 40.68; N = 4.75; I = 43.05 per cent.). It is similar to *esoline methyl ether dimethiodide* in properties, but has a slightly greater solubility in methyl alcohol. Unlike *eseroline* and *eserethole*, it is optically inactive.

When larger quantities of this compound were subsequently required for further work, it was found that by heating the reaction mixture for as long as seven hours and then allowing it to stand over-night before filtering, yields of more than 50 per cent. of the theoretical could be consistently obtained. It is possible that the yield might be still further improved by employing a larger proportion of sodium, but this point has not so far been tested.

* Fusion with sodium carbonate according to Hofmann and Roth, *Ber.*, 1910, 43, 682.

Esoline Ethyl Ether Dimethoperchlorate, $C_{20}H_{36}O_2N_2(ClO_4)_2$, is prepared by the action of perchloric acid on a solution of the diquaternary hydroxide. It is sparingly soluble in water or alcohol. When recrystallised from the former solvent, it forms prisms which melt at $272-273^\circ$ [Found: Cl = 13.26 (Carius), 13.10 (fusion). $C_{20}H_{36}O_2N_2(ClO_4)_2$ requires Cl = 13.27 per cent.].

Eseroline Ethiodide, $C_{13}H_{18}ON_2C_2H_5I$.—One gram of eseroline was dissolved in ethyl iodide and allowed to stand for two days. The crystalline substance which had separated was filtered and washed with ether (yield 1.7 grams). It was recrystallised by dissolving in the minimum amount of hot alcohol and then adding hot ethyl acetate until a faint turbidity appeared. On cooling, it crystallised in radiating needles which melted at 172° (Found: I = 34.49. $C_{13}H_{18}ON_2C_2H_5I$ requires I = 33.96 per cent.).

Esoline methyl ether methyl ethyl diquaternary iodide, $C_{20}H_{16}O_2N_2I_2$, was prepared by the method employed for esoline methyl ether dimethiodide. When recrystallised from methyl alcohol, it forms radiating aggregates which decompose at about 212° . It is evidently isomeric with esoline ethyl ether dimethiodide (Found: C = 40.49, H = 6.23. $C_{20}H_{36}O_2N_2I_2$ requires C = 40.68; H = 6.10 per cent.).

Esoline Ethyl Ether Methyl Ethyl Diquaternary Iodide, $C_{21}H_{38}O_2N_2I_2$.—Eserethole ethiodide was first prepared by dissolving eserethole in ethyl iodide and allowing the solution to stand for some days. The eserethole ethiodide which had separated was filtered and washed with ether. It can be recrystallised, either from a mixture of methyl alcohol and ethyl acetate or by slow precipitation by addition of dry ether to a solution in alcohol. In the present case, however, purification was not attempted, but the crude product was used for the preparation of esoline ethyl ether methyl ethyl diquaternary iodide. The method employed was identical with that used for the preparation of esoline ethyl ether dimethiodide. *Esoline ethyl ether methyl ethyl diquaternary iodide* crystallises from water or methyl alcohol in prisms which melt at about 201° with decomposition. If a concentrated aqueous solution is cooled rapidly, it sets to a gel (Found: C = 41.92; H = 6.30; I = 42.10. $C_{21}H_{38}O_2N_2I_2$ requires C = 41.72; H = 6.29; I = 42.05 per cent.).

Esoline Dimethiodide, $C_{16}H_{32}O_2N_2I_2$.—0.5 Gram of esoline ethyl ether dimethiodide was heated under reflux for half an hour with constant-boiling hydriodic acid. Oily drops of ethyl iodide were formed in the condenser and the characteristic odour of this compound was observed. The hydriodic acid was distilled off under diminished pressure, last traces being removed by the addition of water, which was again distilled off. The residue was then dissolved in methyl alcohol and allowed to crystallise (yield 0.35 gram). After recrystal-

lisation from water, *esoline dimethiodide* forms long prisms which melt at about 212° with decomposition. The presence of a phenolic hydroxy-group is shown by its ready solubility in sodium hydroxide, from which it is reprecipitated on acidification.

The preparation of this compound renders possible the conversion of *esoline ethyl ether dimethiodide* into the corresponding methyl ether. Thus, when *esoline dimethiodide* (prepared from the ethyl ether) is boiled in alcoholic solution with an equivalent of sodium and methyl iodide, it is converted quantitatively into *esoline methyl ether dimethiodide*. The latter compound was identified by its melting point and by analysis (Found: I = 43.99. $C_{19}H_{34}O_2N_2I_2$ requires I = 44.10 per cent.). This clearly demonstrates the relationship which exists between ethyl- and methyl-*esoline dimethiodides*.

Degradation of Esoline Ethyl Ether Dimethiodide by Hofmann's Method.—A hot aqueous solution of 2 grams of *esoline ethyl ether dimethiodide* was treated with excess of moist, freshly precipitated silver oxide, filtered, and the filtrate evaporated to dryness under diminished pressure. The residue formed a brown syrup having a faintly basic odour. It was transferred to a flask and distilled under diminished pressure. The flask was fitted with a capillary which allowed a slow stream of air to pass through the apparatus and thus sweep out the whole of the volatile amine produced, into hydrochloric acid contained in a vessel attached to the receiver. At about $160^{\circ}/12$ mm. an obvious decomposition occurred and at $200^{\circ}/12$ mm. an almost colourless oil distilled over (yield 0.55 gram). The hydrochloric acid was evaporated to dryness on a water-bath, and there was thus obtained 0.16 gram of the hydrochloride of a volatile amine. This was identified as trimethylamine hydrochloride by the following tests: it was very hygroscopic and after crystallisation from alcohol melted at 276° . A portion was converted into the picrate which, after recrystallisation, melted at 218° . The remainder of the hydrochloride was converted into the chloroplatinate and analysed [Found: Pt = 36.89. $(Me_3N)_2H_2PtCl_6$ requires Pt = 36.70 per cent.].

The oily distillate on treatment with aqueous picric acid gave a semi-solid picrate. This was collected and boiled with alcohol, when it became crystalline. It was recrystallised from alcohol, in which it was only sparingly soluble, and formed prisms and spherocrystals which melted at $208-210^{\circ}$ (Found: C = 46.87; H = 4.22. $C_{18}H_{30}O_2N_2 \cdot 2C_6H_3O_7N_3$ requires C = 47.12; H = 4.71 per cent.).

In a second experiment, 6 grams of *ethylesoline dimethiodide* were converted into the quaternary hydroxide, which was distilled

as rapidly as possible at 12 mm. Two grams of an almost colourless oil were collected. This was dissolved in ether and extracted with 1 per cent. hydrochloric acid. The ethereal solution, after drying over sodium sulphate, left on evaporation 0.2 gram of a non-basic oil. Addition of sodium hydroxide to the acid solution precipitated a basic oil, which was shaken out with ether. The ethereal extract was dried over sodium sulphate and the solution filtered. Methyl iodide was then added, when a precipitate slowly formed (yield 0.6 gram). After filtration, it was recrystallised from ethyl acetate and formed plates which melted at 17.2° and then solidified without melting again up to 270° (Found: C = 50.51; H = 7.62; N = 8.15; I = 30.82. $C_{16}H_{28}ON_2 \cdot C_2H_5I$ requires C = 50.24; H = 7.63; N = 6.90; I = 31.28 per cent.).

The ethereal mother-liquors from the preparation of this methyl iodide were evaporated and the residue was heated with methyl iodide. A solid separated which, after filtration, was recrystallised from ethyl acetate. It melted at 146° . Only sufficient was obtained for an iodine estimation (Found: I = 35.7 per cent.). It appears probable that this iodide was identical with the one obtained above, but was contaminated with small quantities of the corresponding diquaternary iodide. The composition of neither substance can as yet be interpreted.

Action of Nitric Acid on Esoline Ethyl Ether Dimethiodide.—When this salt is boiled with concentrated nitric acid, it is converted partly into the corresponding diquaternary nitrate and partly into iodoesoline ethyl ether dimethonitrate. Thus, in one experiment, 1 gram of esoline ethyl ether dimethiodide was gently boiled for four minutes with 1 c.c. of concentrated nitric acid. During this time the greater part of the iodine liberated was expelled. The reaction was then stopped by dilution with water and last traces of iodine were expelled by again boiling. The solution was evaporated to dryness on a water-bath, when a residue was obtained consisting of a mass of crystals contaminated with a yellow oil. The latter was almost completely removed by boiling with acetone, in which the crystals were sparingly soluble. Recrystallisation of the product could be effected from alcohol, in which it is rather soluble, or better from a mixture of alcohol and ethyl acetate, or by slow precipitation from alcoholic solution by ether. The substance so obtained formed pale yellow needles which melted at 241° with decomposition. It was, however, evidently contaminated with esoline ethyl ether dimethonitrate, for no analyses could be obtained which agreed with the formula $(C_{20}H_{35}ON_2I)(NO_3)_2$. That it consisted mainly of this product was, however, proved by its conversion into iodoesoline ethyl ether dimethiodide by

double decomposition with potassium iodide. This was carried out in the following manner: the crude nitrate obtained from 1 gram of esoline ethyl ether dimethiodide was dissolved in water and solid potassium iodide was added to the solution. The diquaternary iodide commenced to separate almost immediately. After warming to ensure solution of the potassium iodide, the periodide which had formed was filtered and washed thoroughly with water, in which it was very sparingly soluble. It was then suspended in water and the latter saturated with sulphur dioxide. The solution was boiled until it was pale yellow and all the sulphur dioxide had been driven off. On cooling, the diquaternary iodide crystallised out (yield 0.75 gram). It was recrystallised from ethyl alcohol and again from water and formed faintly yellow, long prisms which melted at about 225° with decomposition. Even after repeated crystallisation it retained its creamy colour. *Iodoesoline ethyl ether dimethiodide* is sparingly soluble in cold water and in most organic solvents and is consequently very readily purified [Found: C = 33.86, 33.88; H = 5.18, 5.04; *N = 4.65; I ionic, = 34.49, and hence total I = $\frac{3}{2} \times$ ionic I = 53.23. $C_{26}H_{33}O_2N_2I_3$ requires C = 33.52; H = 4.88; N = 3.91; I = 53.21 per cent.].

Hydroxyesoline Dimethiodide, $(C_{18}H_{32}O_3N_2I_2)$.—Two grams of iodoesoline ethyl ether dimethiodide were heated under reflux for forty-five minutes with an excess of constant-boiling hydriodic acid. Solution gradually took place, ethyl iodide being at the same time produced, as shown by the condensation of oily drops in the condenser and by the characteristic odour of this substance. Removal of the hydriodic acid by distillation under diminished pressure left a black, sticky residue of periodide. This was dissolved in hot methyl alcohol and the solution so obtained was saturated with sulphur dioxide. Addition of a few c.c. of water produced almost complete decoloration (removal of iodine can also be effected by boiling the methyl alcoholic solution with finely divided copper). The solution was then evaporated to a small bulk. Crystallisation gradually took place on cooling. The solid was filtered and washed with a small quantity of ethyl alcohol, in which it is much less soluble than in methyl alcohol (yield 1.1 grams). It was recrystallised first from a mixture of ethyl and methyl alcohols and finally from water. *Hydroxyesoline dimethiodide* forms prisms which melt at about 212° with decomposition. Its phenolic properties are shown by its ready solubility in sodium hydroxide, from which solution it is reprecipitated on acidification (Found: C = 37.50; H = 5.79; I = 43.91. $C_{18}H_{32}O_3N_2I_2$ requires C = 37.37; H = 5.54; I = 43.94 per cent.). The same substance may be

* By Dumas's method; nitrogen contained nitric oxide; see introduction.

produced by the action of fuming hydrobromic acid. Thus, 0.5 gram of iodoesoline ethyl ether dimethiodide was heated for two hours at 120° in a sealed tube. The hydrobromic acid was distilled off under diminished pressure and the residue dissolved in water and filtered from a small quantity of periodide. Addition of potassium iodide to the filtrate caused the hydroxyesoline dimethiodide to separate. This was filtered and recrystallised and was found to be identical with that obtained above (Found: C = 37.67; H = 5.77 per cent.). It should be recorded that this specimen was slightly brown in colour and gave a green coloration with ferric chloride which changed to reddish-brown on the addition of sodium carbonate. This "catechol" reaction was, however, undoubtedly due to the presence of a slight impurity, since it was not given by other specimens, and is identical with a reaction described by Straus for physostigmol.

Hydroxyesoline Ethyl Ether Dimethiodide, $C_{20}H_{36}O_3N_2I_2$.—0.45 Gram of hydroxyesoline dimethiodide was dissolved in 4 c.c. of a solution of 0.5 gram of sodium in 50 c.c. of ethyl alcohol (slightly more than two equivalents of sodium were thus employed). The solution became slightly green in colour. Ethyl iodide was then added and the mixture heated on the water-bath for one hour. During this time a yellow solid separated, which was filtered off after cooling (yield 0.37 gram). It was recrystallised from a mixture of ethyl and methyl alcohols and formed aggregates and torpedo-shaped prisms which were slightly yellow in colour and melted at about 205° with decomposition. That ethylation had taken place was clearly shown by the fact that its solubility was no greater in sodium hydroxide than in water. It also differed obviously from iodoesoline ethyl ether dimethiodide. Thus its solubility in water and methyl alcohol was much greater and its crystalline form and melting point were quite different (Found: I = 42.11. $C_{20}H_{36}O_3N_2I_2$ requires I = 41.91 per cent.). The production of this compound demonstrates that the second hydroxy-group introduced into the esoline molecule is non-phenolic in properties.

Action of Nitric Acid on Esoline Methyl Ether Dimethiodide.—When methylesoline dimethiodide is treated with nitric acid in the manner described above in the case of the corresponding ethyl compound, it is converted into iodoesoline methyl ether dimethiodide. This substance is much less soluble in water than the corresponding ethyl ether and can be readily crystallised from this solvent. It forms pale yellow, flat prisms which melt with decomposition at about 255° . When treated with potassium iodide, it is converted into the dimethiodide. *Iodoesoline methyl ether dimethiodide* is sparingly soluble in both methyl and ethyl alcohol,

but can be readily recrystallised from water. It forms pale yellow, flat prisms which melt with decomposition at about 237° [Found: C = 32.76; H lost; I(ionic) = 36.14, hence I(total) = $\frac{3}{2} \times$ ionic I = 54.21; I(total, by Carius) = 53.69. $C_{19}H_{33}O_2N_2I_3$ requires C = 32.48; I = 54.27 per cent.].

Preparation of Esoline Ethyl Ether Dimethiodide from Eseretholemethine.—To 0.67 gram of eseretholemethine, dissolved in methyl iodide, were added 5 c.c. of a solution of 0.5 gram of sodium in 25 c.c. of ethyl alcohol, and the mixture so obtained was heated under reflux for four hours on a water-bath. After this time, the solution was cooled, but no separation of solid occurred. On seeding, however, with a minute crystal of esoline ethyl ether dimethiodide, crystallisation gradually took place. The substance was filtered (yield 0.57 gram) and recrystallised from methyl alcohol. The product so obtained was identical with esoline ethyl ether dimethiodide. Evidently eseretholemethine is an intermediate product in the production of this compound from eserethole methiodide.

We wish to record our thanks to the administrators of the Carnegie Trust for the Scottish Universities for a grant, which alone is making this expensive research possible.

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[Received, February 27th, 1923.]

XC.—*Spinacene: its Oxidation and Decomposition.*

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SINCE the publication of my previous paper on spinacene (T., 1918, 113, 458), I have been successful in obtaining a considerable quantity of the shark liver oil, and have prepared from it further and larger quantities of spinacene.

The more important physical properties of the hydrocarbon are recorded in the previous paper, but it seems desirable that the following results, obtained with a larger and purer specimen, should be recorded: d_{20}^{20} 0.8588, n_D^{20} 1.4951.

The specific refraction of the hydrocarbon calculated by the $(n^2 - 1)/(n^2 + 2)d$ expression is 0.3396, and the molecular refraction 134.5. Taking Conrady's average numbers for the atomic specific refractions (D-line), $C_{29}H_{48}$ with six ethenoid linkings requires $[R_L]$ 133.7.

I have also determined the heat of combustion in a Mahler bomb,

and obtained in two experiments, the numbers 4,388 and 4,372 molecular gram-calories, respectively.

Hydrogenation of Spinacene.—Since in my earlier experiments, the amount of spinacene available was small, and the saturated hydrocarbon was not obtained pure, I have prepared a further quantity. Dried hydrogen was passed as before through spinacene heated at about 200° , using active platinum black as the catalyst, and at the end of about fifty hours complete saturation was obtained. After the removal of the platinum, the resulting oil was distilled, when practically the whole boiled between $280\text{--}281^{\circ}$ (corr.)/24 mm. The fraction so obtained was a colourless, slightly viscous liquid, completely devoid of odour (Found: C = 85.25; H = 14.77. $\text{C}_{29}\text{H}_{60}$ requires C = 85.29; H = 14.71 per cent.). It was optically inactive.

The density of the hydrocarbon at $15^{\circ}/15^{\circ} = 0.8144$, and at $20^{\circ}/20^{\circ} = 0.8119$. The value of $n_D^{20} = 1.4532$. Its specific refraction is therefore 0.3330, and its molecular refraction 135.8. The theoretical number for a saturated hydrocarbon having the formula $\text{C}_{29}\text{H}_{60}$ is 135.5.

Two determinations of the heat of combustion in the Mahler bomb gave 4,541 and 4,538 molecular gram-calories, respectively. The values recorded for the heats of combustion of carbon and hydrogen vary within somewhat considerable limits, but whichever results are taken the calculated value for the heat of combustion of a normal paraffin $\text{C}_{29}\text{H}_{60}$ would be considerably in excess of that found for the saturated hydrocarbon from spinacene, which is, of course, not a normal paraffin. This would appear to support the view of Fajans (*Z. physikal. Chem.*, 1921, **99**, 395) that saturated hydrocarbons with side chains have lower heats of combustion than the isomeric straight-chain compounds.

It also appears that the average thermochemical value for each of the six ethenoid linkings of spinacene is very near the value obtained for compounds of lower molecular weight. I propose the name *spinacene* for this saturated hydrocarbon as indicating its relationship to spinacene.

Spinacene Dodecaboride.—I have directed attention (*loc. cit.*) to the fact that not only were all the physical constants of spinacene in good agreement with the formula $\text{C}_{29}\text{H}_{48}$, but that, with one exception, the composition of the various compounds of this hydrocarbon was in better accord with that formula than with the formula $\text{C}_{30}\text{H}_{50}$ which I had previously been led to assign to it. The single exception to which I have referred was the dodecaboride. I did not, however, attach very great importance to this discrepancy inasmuch as the action of bromine on spinacene

is very complicated, and it seemed possible that the compound I had analysed might not have been entirely homogeneous. In order to clear up this point I have prepared a further and larger quantity of the dodecaboride in the manner already described.

When bromine is allowed to react with spinacene in ether solution, several successive crops of crystalline material can be obtained. In my earlier work, no steps were taken to separate the compound which crystallises out within, say, an hour of the addition of the bromine, from that which separates on standing for a longer time. In the present case, however, the crystalline material separating during the first hour was filtered off, washed with ether, and purified by repeated crystallisation from a mixture of tetrachloroethane and alcohol. The percentage of bromine rose from 70.0 in the original preparation to 70.88 after two recrystallisations, at which point it remained constant.

As $C_{30}H_{50}Br_{12}$ requires $Br = 70.07$ and $C_{29}H_{48}Br_{12}$ requires $Br = 70.79$, it will be seen that the dodecaboride contains almost exactly the amount of bromine required for the lower formula, and therefore comes into line with all the other compounds of spinacene. This experiment, therefore, removes the last remaining doubt as to the formula of the hydrocarbon.

Oxidation of Spinacene.—Many attempts were made to oxidise spinacene in the hope that products might have been obtained which would throw some light on its constitution. Among the oxidising agents chromic acid, potassium permanganate in acid and in alkaline solutions, potassium permanganate in acetone solution, nitric acid, oxygen in the presence of a catalyst, benzoyl peroxide, and hydrogen peroxide were tried.

An interesting point in connexion with these experiments was the remarkable stability shown by spinacene to the majority of the above oxidising agents, notwithstanding its highly unsaturated character. Thus, aqueous solutions of chromic acid appeared to have no effect on spinacene until their concentrations reached a point at which the destruction of the hydrocarbon occurred. The same behaviour was exhibited by permanganate, both in acid and in alkaline solutions. In the presence of alkali the permanganate acted more readily than in acid solution, and a little acetone together with a trace of some fragrant ketone was obtained. The great bulk of the hydrocarbon, however, remained either unacted upon, or was completely destroyed, according to the concentration of the permanganate. The addition of powdered potassium permanganate to an acetone solution of spinacene failed to give more encouraging results.

Action of Nitric Acid.—In a previous communication (*loc. cit.*),

I pointed out that with nitric acid spinacene appeared to undergo nitration and oxidation simultaneously. Fresh experiments have confirmed that observation, and have incidentally afforded a further example of the stability of the hydrocarbon. Spinacene can, in fact, be dissolved in a mixture of equal parts of strong sulphuric and nitric acids without any apparent decomposition or evolution of nitrous fumes, provided the temperature of the mixture be not allowed to rise too high during the addition.

On pouring the products of the reaction into water, a large yield of a yellow substance was obtained, very similar in its composition and general character to that obtained previously by the action of dilute nitric acid alone. Whether this consists of a single substance or a mixture of substances is not at present known.

Action of Benzoyl Peroxide.—When benzoyl peroxide was added to a solution of spinacene in glacial acetic acid, a vigorous reaction occurred on warming, and on pouring into an excess of ammonia a white amorphous oxidation product was obtained. Inasmuch as subsequent experiments showed that this was very similar in character to the product formed by the action of hydrogen peroxide, and as the latter method presented certain advantages, the benzoyl peroxide reaction was not further studied.

Action of Hydrogen Peroxide.—The strongest solutions of hydrogen peroxide commercially obtainable are without action on spinacene. In the absence of water, however, oxidation readily occurs. To a solution of 100 volume hydrogen peroxide sufficient acetic anhydride was added to react with the whole of the water present. This solution (230 c.c.) was added little by little to a hot solution of spinacene (35 c.c.) in glacial acetic acid (75 c.c.). An immediate reaction occurred with the development, as a rule, of sufficient heat to maintain the temperature of the liquid at the required point. Occasionally, however, it was found necessary to apply a little external heat. When the reaction following the addition of the last portion of the oxidising solution had subsided, the liquid was heated for about ten minutes, and the solution after cooling was then poured slowly into a solution of sodium hydroxide, containing considerably more alkali than was necessary to neutralise the whole of the acid. The precipitate which formed consisted of a white, amorphous substance. This was separated, washed as completely as possible with ice-cold water, and dried in an exhausted desiccator over sulphuric acid. The dried product was then ground, washed once more with ice-cold water, and dried as before to a constant weight.

As it was subsequently discovered that caustic alkali had some action on the oxidation product, a large volume of iced water was

substituted for the alkaline solution. This had the further advantage of yielding a more granular precipitate and one which could be more easily handled.

Three different preparations gave the following results : C = 64.8, 64.7, 64.9; H = 9.4, 9.4, 9.3. $C_{27}H_{48}O_8$ requires C = 64.8; H = 9.6 per cent. When this compound was dissolved in glacial acetic acid and again treated with hydrogen peroxide, it was recovered in a somewhat whiter condition, but its composition remained unaltered. It would appear, therefore, that this is a definite end product of the oxidation by this means.

Products containing less oxygen were isolated in some instances, but these were obviously mixtures with intermediate compounds. This substance is white, resinous, and insoluble in water. It has no sharp melting point, but begins to soften at about 40°, with decomposition. Owing to its marked tendency to form colloidal solutions, molecular weight determinations by the cryoscopic method were in all cases too high. In glacial acetic acid, for example, results indicating about 600 were obtained, but in benzene, in which the solutions were more markedly colloidal, results were obtained as high as 850. The formula given above requires $M = 500$. This behaviour is very similar to that observed in the case of attempts to determine the molecular weight of abietic acid in the above two solvents.

Having regard to the method of preparation of this substance, it was thought desirable to examine it for the presence of acetyl groups. These were found to be absent. It is saturated, and appears to be in the nature of an organic peroxide. The peroxide properties, however, are not very strongly marked since, although the compound liberates iodine from potassium iodide, the quantity so liberated is not sufficient to account for even one normally reacting peroxide group. In this respect it resembles many typical autoxidation products (Engler and Weissberg, "Vorgänge der Autoxydation").

It would also appear to resemble very closely, if not to be identical with, the solid product formed when spinacene is exposed to air. Direct measurements showed that spinacene in these circumstances is capable of uniting with about 25 per cent. of its weight of oxygen. As in the case of linseed oil, however, volatile products are formed at the same time, so that the true oxygen absorption is really somewhat greater than that actually measured. Moureu and Dufraisse (*Compt. rend.*, 1922, 174, 258) made the interesting observation that certain substances, notably quinol, even when present in traces, have the effect of preventing the atmospheric oxidation of certain unsaturated compounds. I

thought, therefore, it might be desirable to ascertain how spinacene would behave. When little more than a trace of quinol was added to spinacene, and the latter exposed to an atmosphere of oxygen, the weight remained practically constant, showing that there had been no absorption of oxygen. At the end of several months, the spinacene was as fluid as at the commencement of the experiment, whilst in a control experiment, the spinacene had become converted into a solid oxidation product at the end of a few weeks.

Although spinacene itself is very resistant to the action of most oxidising agents, the oxidation product above described readily undergoes further oxidation when treated with permanganate, especially in the presence of a little alkali. Thus, when it was treated gradually with an aqueous solution of potassium permanganate (1 per cent.) and vigorously shaken, oxidation readily occurred. When the reduction of the permanganate became slow, the oxides of manganese were filtered off, and the clear filtrate was concentrated and acidified with very dilute hydrochloric acid. A white, granular precipitate formed, which when washed and dried over sulphuric acid in an exhausted desiccator had the following composition (average of four closely agreeing analyses of four different preparations): C = 65.62; H = 9.79. $C_{25}H_{44}O_7$ requires C = 65.78; H = 9.65 per cent. This substance, which proved to be an acid, was prepared from a number of different preparations of the peroxide product, and the analytical results in all cases agreed very closely. It may, therefore, I think, be regarded as a definite compound. Its molecular weight was difficult to determine by the cryoscopic method, the results of several determinations ranging from 400 to 500. $C_{25}H_{44}O_7$ requires $M = 456$. Attempts to determine the molecular weight by titration with standard alkali tended to confirm the above molecular weight, but definite results were difficult to obtain owing to the fact that the acid is acted upon by an excess of alkali. When the peroxide oxidation product is allowed to stand in contact with aqueous alkali it undergoes decomposition with the formation of an acid, which could not, however, be obtained in a condition pure enough for analysis.

Decomposition of Spinacene by Heat.—The results obtained by distilling spinacene under a pressure of about 45 mm. in the presence of a small quantity of metallic sodium have been described (*loc. cit.*), and this experiment has been repeated. As before, a great deal of polymerisation occurred, but the main product distilling over consisted of a cyclodihydroterpene, having properties closely agreeing with those of the compound previously described. Many attempts were made under varying conditions to prepare a definite bromine

derivative of this hydrocarbon, but in every case an oil was obtained from which crystals did not separate even on long standing. Inasmuch as the sodium appeared to bring about so much polymerisation, I endeavoured to secure decomposition of the spinacene by heat in another manner. To this end, the spinacene was distilled from a Wurtz flask with a long and wide neck. In this neck there was suspended a small grid of fine platinum wire which could be kept at any required temperature by means of an electric current. In this apparatus the spinacene could be distilled under any required pressure and the vapours compelled to pass over the heated platinum surface. In practice, it was found best to maintain the pressure in the flask at about 45 mm. and to keep the platinum grid at a dull red heat throughout the experiment. A U-tube containing high-boiling liquid paraffin, and surrounded by a freezing mixture, was introduced into the condensing system after the ordinary water condensers, and arrangements were also made for collecting gaseous products.

The product, condensed by the water condenser, consisted of a yellow, mobile liquid, more than half of which was found to be distillable with steam, the remainder consisting chiefly of unchanged spinacene. The steam-distilled portion was submitted to fractional distillation under reduced pressure, and was found to consist almost entirely of a substance boiling at $79-83^{\circ}/33$ mm. (Found: $C = 86.7$; $H = 13.2$. $C_{10}H_{18}$ requires $C = 87.0$; $H = 13.0$ per cent.). This hydrocarbon consists of a yellow liquid having a smell strongly suggestive of the lower olefines. Inasmuch as the yellow colour persists after steam distillation and other methods of purification, it would appear to be a constitutional property. The possibility, however, of the presence of a small proportion of some highly coloured hydrocarbon is not entirely excluded. It boils at $160-167^{\circ}/750$ mm., the liquid becoming discoloured, and ultimately viscous owing to polymerisation. It is optically inactive.

A molecular-weight determination in benzene gave the following results: 0.4683 in 13.568 benzene gave $\Delta t = -1.265$. $M = 136$. $C_{10}H_{18}$ requires $M = 138$. It has $d_{15}^{20} 0.8025$ and $d_{20}^{20} 0.8008$. $n_D^{15} 1.4606$ and $n_D^{20} 1.4584$. Its specific refraction, calculated by the n_D^2 formula, is 0.341 , and the molecular refraction 47.1 . Taking Conrady's average numbers for the atomic specific refractions (D-line), $C_{10}H_{18}$ with two ethenoid linkings requires 47.5 .

A determination of the amount of iodine with which this compound is capable of uniting gave a value of 347 , the theoretical number for $C_{10}H_{18}$ with two ethenoid linkings being 368 parts per cent.

Bromine absorption estimations were also made, and it was found in a number of experiments that the values corresponded

with an addition of between three and four atoms of bromine for each molecule of the hydrocarbon. It will be seen, therefore, that this hydrocarbon has the properties of a diolefine, whilst the hydrocarbon obtained by heating spinacene in the presence of sodium is a *cyclo*-compound of the same molecular formula. The bromine estimations, as well as the other results, appear to indicate that it is not easy to obtain either of these two compounds in a quite pure condition, but that each is very apt to contain a little of the other. There can, I think, be very little doubt that they are closely related, but attempts to convert the olefinic hydrocarbon into the *cyclo*-compound have not, so far, been successful.

Bromine Derivative.—The hydrocarbon was dissolved in five times its weight of a mixture of ether (4 parts) and amyl alcohol (1 part). A solution of bromine in the same mixed solvent was added slowly, and the liquid kept cool in a freezing mixture. After standing for twelve hours, the greater part of the solvent was allowed to evaporate at the ordinary temperature. When the remaining liquid was allowed to stand, crystals formed slowly and after a time a dense oil separated. The yield of this crystalline compound was very small, and whether crystals are obtained or not appears to depend very much upon the precise conditions under which the experiment is carried out. The colourless crystals obtained by recrystallising from a mixture of ether and amyl alcohol and drying to constant weight in an exhausted desiccator over sulphuric acid melted at 136° (corr.) (Found: Br = 69.64. $C_{10}H_{18}Br_4$ requires Br = 69.87 per cent.).

A molecular-weight determination in benzene was made:

0.1904 in 10.6917 benzene gave $\Delta t = -0.195^{\circ}$. $M = 456$.
 $C_{10}H_{18}Br_4$ requires $M = 458$.

In the fractional distillation of the products from which this olefinic hydrocarbon was obtained there occurred a small fraction, boiling under atmospheric pressure between 40° and 50° , and on distilling the high boiling paraffin, used for trapping low-boiling compounds formed during the decomposition of the spinacene by heat, a larger quantity of a fraction, boiling within the same range of temperature, was obtained.

On further distillation, this was resolved into two fractions, one boiling under atmospheric pressure at $40-45^{\circ}$, and the other at $45-50^{\circ}$. These had d_{20}^{20} 0.6800 and 0.6846, respectively, and n_D^{25} 1.4170 and 1.4186. The specific refraction of the lower of the two fractions (b. p. $40-45^{\circ}$), calculated by the n^2 formula, = 0.571. The calculated specific refraction of isoprene (C_5H_8) = 0.300, and of amylene (C_5H_{10}) = 0.354.

As neither of these fractions appeared to consist of a single

compound, and as the physical properties and the numbers given on analysis were very similar, it was decided to mix them together for purposes of further examination. The following are the results of analyses (Found : C = 87.20, 87.19; H = 13.20, 13.20. C_5H_8 requires C = 88.2; H = 11.8. C_5H_{10} requires C = 85.7; H = 14.3 per cent.).

A molecular-weight determination in benzene gave the following results :

0.1955 in 13.799 benzene gave $\Delta t = -0.948^\circ$. $M = 74$. (C_5H_8 requires $M = 68$. C_5H_{10} requires $M = 70$).

A determination of the iodine absorption by the Wijs method gave a value of 344, the theoretical number for C_5H_{10} with one ethenoid linking being 362. The calculated value for isoprene, on the other hand, is 741, but it has recently been shown by Faragher, Gruse, and Garner (*J. Ind. Eng. Chem.*, 1921, **13**, 1044) that the number actually obtained with isoprene by the Wijs method is 382. The iodine value is not, therefore, very conclusive in regard to the presence or absence of some C_5H_8 hydrocarbon in this fraction. These results appear to indicate that this fraction consists of one or more of the amylene with a proportion of some C_5H_8 hydrocarbon, probably isoprene.

In addition to the above substances formed during the decomposition of spinacene by heat, a certain amount of gas was collected. This gas, on analysis, was found to contain about 75 per cent. of unsaturated (olefinic) and about 25 per cent. of saturated (paraffin) hydrocarbons. The composition, however, varied somewhat according to the precise conditions of the experiment.

Of the two $C_{10}H_{18}$ hydrocarbons resulting from the decomposition of spinacene by heat, the *cyclo*-form, at least, has undoubtedly been obtained in a nearly pure condition. For purposes of identification, therefore, considerable reliance may safely be placed upon the correctness of its physical properties as recorded in my previous communication. In that communication I expressed the opinion that this hydrocarbon might prove to be *cyclodihydromyrcene* or *cyclolinaloolene*. Recent work has shown that these two hydrocarbons may be identical, but whether that is the case or not, the hydrocarbon obtained from spinacene differs from either, since it does not yield any levulinic acid or other keto-acid on oxidation.

On the other hand, its physical properties agree very closely with those assigned by Wallach (*Annalen*, 1908, **360**, 34) to certain *cyclohexane* derivatives containing a semi-cyclic double linkage.

The following are three of the compounds of this series, together with their chief physical properties, which the hydrocarbon from spinacene most closely resembles. Under (4) I have given, for

The above formula is not intended to represent anything more than an outline of the structure of spinacene, but it appears to explain satisfactorily the properties of that hydrocarbon so far as these are at present known.

Certain of the properties of spinacene might, perhaps, be more readily explained by an alternative formula with two terminal unsaturated isopropyl groupings, but although such a formula is not entirely excluded it is, in my opinion, less probable than the one I have given above.

In conclusion, I desire to express my best thanks to Mr. J. J. Scanlan, A.R.C.Sc.I., A.I.C., for much valuable help in connexion with this investigation.

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[Received, January 26th, 1923.]

XCI.—*The Molecular Configurations of Polynuclear Aromatic Compounds. Part II. 4:6:4'-Trinitrodiphenic Acid and its Resolution into Optically Active Components.*

By GEORGE HALLATT CHRISTIE and JAMES KENNER.

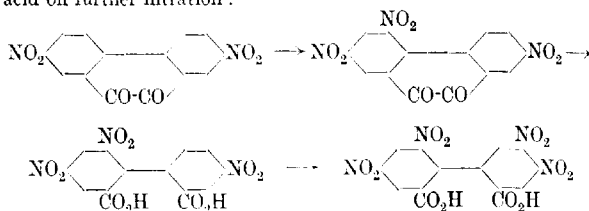
INASMUCH as two forms of 6:6'-dinitrodiphenic acid exist (Kenner and Stubbings, T., 1921, **119**, 593), it might have been expected that isomeric tetranitrodiphenic acids would result from the nitration of these isomerides. Experiment showed, however, that both the dinitro-acids furnish the same tetranitrodiphenic acid (Christie and Kenner, T., 1922, **121**, 614), and as this acid, like the γ -6:6'-dinitrodiphenic acid, is also obtained by synthesis from the appropriate chlorodinitrobenzoic acid and is resolvable into optically active components, it appears to correspond to the γ - rather than to the β -dinitrodiphenic acid.

In the hope of supplying a further instance of the type of isomerism in question, it was decided to attempt the preparation of a second form of 4:6:4':6'-tetranitrodiphenic acid. The most likely method of achieving this appeared to be by oxidation of 2:4:5:7-tetranitrophenanthraquinone, since the above β -acid is obtained in this manner from 4:5-dinitrophenanthraquinone. An unexpected difficulty encountered in the preparation of the necessary tetranitrophenanthraquinone has, however, so far prevented the realisation of this object.

Although, as above mentioned, tetranitrodiphenic acid is readily

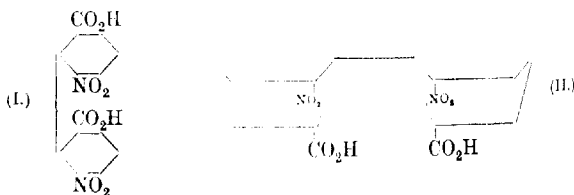
obtained from the dinitro-acids, we found that, under similar conditions, 2:7- and 4:5-dinitrophenanthraquinones only furnish trinitro-derivatives, and this result was not modified when still more vigorous methods of nitration were employed. The reason for this is a matter requiring further investigation, more especially as the orientation of the entering nitro-group in each case is in accordance with anticipation, and it is not clear why the second benzene nucleus does not undergo nitration in the same manner as the first.

The product obtained from 2:7-dinitrophenanthraquinone is 2:4:7-trinitrophenanthraquinone, since the 4:6:4'-trinitrodiphenic acid obtained from it by oxidation furnishes the above tetranitro-acid on further nitration:



Exactly analogous results were obtained from the 4:5-dinitroquinone, and will be described in a future communication.

Although the outcome of these experiments frustrated the purpose with which they were undertaken, 4:6:4'-trinitrodiphenic acid itself is of interest in connexion with the general theme of this series of papers. For, although there is a strong presumption that the isomerism of the two dinitrodiphenic acids is stereochemical rather than structural, more definite evidence on this point would be welcome, and yet is not necessarily obtainable from an examination of β-dinitrodiphenic acid. Thus, failure to resolve this acid into optically active components would be equally explicable as due to a plane configuration of the molecule, corresponding to the formula as ordinarily written, or to the acid being a *cis*-compound with a non-coplanar arrangement of its benzene nuclei, such that the formula exhibits a plane of symmetry. Examples of such



formulae are shown in (I) and (II), based, respectively, on the Kauler formula for diphenyl and on one of the formulae suggested by Sachse (*Ber.*, 1888, **21**, 2530) for benzene, and obvious modifications will suggest themselves. If, however, 4:6:4'-trinitrodiphenic acid be of the same type as β -dinitrodiphenic acid, these alternatives would not be equivalent in respect of resolvability of the acid. For, owing to the dissimilarity of the two substituted phenyl nuclei, a *cis*-non-planar molecular configuration would render the acid resolvable, but this would not apply in the case of a plane configuration. The resolution of 4:6:4'-trinitrodiphenic acid, which has now been accomplished, is therefore, subject to the reservation mentioned, evidence in favour of the view that both the 6:6'-dinitrodiphenic acids are to be represented by non-planar formulae. These, it need scarcely be pointed out, are not necessarily, although perhaps very probably, of the same type.

A fairly sharp resolution of γ -6:6'-di- and of 4:6:4':6'-tetranitrodiphenic acids was accomplished by means of their brucine salts, but in the present instance this was by no means the case.* The less soluble brucine salt, derived from the *d*-form of the acid, was fairly easily obtained in the pure condition, but the *l*-acid was much more satisfactorily prepared through its quinidine salt. The specific rotatory powers of solutions of the respective sodium salts were $+156.8^\circ$ and -130.5° .

This solution also marks a step towards the ascertainment of the conditions, if any, on which the existence of the non-planar configuration of diphenyl derivatives is dependent. Whereas the acids previously resolved each contained besides the two carboxyl groups, two nitro-groups in the 6:6'-position, the acid now investigated contains only one, and this suffices to ensure the stability necessary for the existence of optically active forms.

We would also direct attention to an interesting property of the above tri- and tetra-nitro-acids, which has doubtless been observed in other cases, but, so far as we are aware, has not received the attention it would seem to deserve. The acids in question are precipitated from solutions of their salts as very viscous oils which only very slowly solidify, although their melting points are high. Solidification is hastened by inoculation, but is still slow and occurs more readily in the cases of the racemic than of the active compounds. The studies by Tammann of the relationship between temperature and the velocity of crystallisation of supercooled

* It may be that this contrast is also an indication of a difference in type, because the pairs of brucine salts derived from 2- and 4-nitrodiphenic acids (obtained from the corresponding quinones) are also somewhat difficultly separable, whilst those from another synthetic acid are readily separated.

liquids are well known, and have an obvious bearing on our observations, but apparently no consideration has been given to molecular configuration as a possible factor in this connexion. It will readily be seen that a non-planar configuration of the molecules concerned would render the fitting together of a number of them to a solid ordered aggregate a somewhat intricate process, likely to require some time for its accomplishment, whether the configuration of the units in the aggregate remain the same as that of the original isolated molecules, or be a modified form of it. This will especially be so in view of the high viscosity of the liquids at the ordinary temperature. Perhaps also for this reason, the products obtained in the attempt to prepare the usual derivatives of 4:6:4':6'-trinitrodiphenic acid were viscous oils, which could not be induced to solidify. It is in accord with these suggestions that when the racemic acids are generated by oxidation in hot solution by a time reaction, permitting of the necessary adjustments of the separate molecules, the solid acids are at once obtained.

EXPERIMENTAL.

4:6:4':6'-Tetranitrodiphenic Acid.

The following analytical data were inadvertently omitted from the previous communication. For the compound of methyl *α*-4:6:4':6'-tetranitrodiphenate with benzene (Found: loss of weight at 130° = 8.02. $C_{16}H_{10}O_{12}N_4 \cdot \frac{1}{2}C_6H_6$ requires C_6H_6 = 7.98 per cent.), and with xylene (Found: loss of weight at 130° = 10.33. $C_{16}H_{10}O_{12}N_4 \cdot \frac{1}{2}C_8H_{10}$ requires C_8H_{10} = 10.52 per cent.). The composition of these two compounds is noteworthy, since out of about 600 compounds discussed by Pfeiffer ("Organische Molekul-Verbindungen," Stuttgart, 1922), that of picric acid with phenol is the only one in which one molecule of the hydrocarbon derivative is associated with two of nitro-compound.

α-4:6:4':6'-Tetranitrodiphenic Acid.—A solution, prepared at the ordinary temperature, of the brucine salt (2.1 grams) previously described in concentrated hydrochloric acid solution (60 c.c.) was repeatedly extracted with ether. The extract, after repeated washing with water to remove brucine and mineral acid, was dried and worked up in the usual manner. The viscous oil obtained required 32.66 c.c. of *N*/10-sodium hydroxide for neutralisation. For a 1.64 per cent. aqueous sodium salt solution so prepared, $[\alpha]_D^{20} = +115^\circ$. The brucine salt prepared by treating a portion of the solution with brucine hydrochloride melted and decomposed at 250° before recrystallisation, so that no appreciable racemisation had occurred in the processes just described.

The free acid was precipitated from a solution of its sodium salt in the form of a yellow oil, which eventually solidified. The air-dried material melted at $53-54^{\circ}$, but resolidified and again melted at $226-227^{\circ}$ [Found: $\text{H}_2\text{O} = 11.37$; equivalent = 238.9. $\text{C}_{12}\text{H}_4\text{O}_8\text{N}_4(\text{CO}_2\text{H})_2 \cdot 3\text{H}_2\text{O}$ requires $\text{H}_2\text{O} = 11.34$ per cent.; equivalent = 238. Found: for the anhydrous acid, equivalent = 211.7. $\text{C}_{12}\text{H}_4\text{O}_8\text{N}_4(\text{CO}_2\text{H})_2$ requires equivalent = 211].

1.4 : 6 : 4' : 6'-*Tetranitrodiphenic acid* was prepared in a similar manner. For a 1.24 per cent. aqueous solution of its sodium salt, $[\alpha]_D = -116^{\circ}$, and the brucine salt prepared from it melted and decomposed at 197° . The free acid, first precipitated as a yellow oil, melted at $52-53^{\circ}$, and again at 226° [Found: $\text{H}_2\text{O} = 11.56$. $\text{C}_{14}\text{H}_6\text{O}_{12}\text{N}_4 \cdot 3\text{H}_2\text{O}$ requires $\text{H}_2\text{O} = 11.34$ per cent. Found: equivalent of the anhydrous acid = 210.3. $\text{C}_{12}\text{H}_4\text{O}_8\text{N}_4(\text{CO}_2\text{H})_2$ requires equivalent = 211].

2 : 4 : 7-*Trinitrophenanthraquinone*.

2 : 7-Dinitrophenanthraquinone (10.5 grams) was heated on the water-bath with nitric acid (50 grams, d 1.5) and sulphuric acid (60 grams) for fourteen hours. When the solution was poured on to ice (200 grams), a precipitate (7.7 grams) was obtained, whilst partial neutralisation of the liquors caused a further quantity (1.4 grams) to separate. The product, after drying⁹ on porous earthenware, crystallised from benzene in shining, yellow, hexagonal prisms, m. p. 203° (Found: loss of weight at $130^{\circ} = 19.05$; $\text{N} = 10.26$. $\text{C}_{14}\text{H}_5\text{O}_8\text{N}_3 \cdot \text{C}_6\text{H}_6$ requires $\text{C}_6\text{H}_6 = 18.53$; $\text{N} = 9.98$ per cent.). The trinitro-quinone has the same melting point when freed from benzene, but its compound with xylene melts first at 125° , and again at $202-203^{\circ}$. By treatment of the quinone with cold 2*N*-sodium hydroxide solution, it is converted into a black, flocculent mass, probably owing to its conversion into trinitrodipheynleneglycollic acid (compare Schmidt and Bauer, *Ber.*, 1905, 38, 3737).

When the above nitration was performed at $150-160^{\circ}$, the trinitro-quinone was again produced, but in one experiment was accompanied by a very small quantity of a product, m. p. 261° , sparingly soluble in benzene. Again, after the dinitro-quinone (1 gram) had been boiled with nitric acid (13.5 c.c., d 1.5) and sulphuric acid (3.4 c.c.) for two and a half hours, it was recovered unchanged.

1.4 : 6 : 4' : 6'-*Trinitrodiphenic Acid*.

2 : 4 : 7-*Trinitrophenanthraquinone* (10.5 grams) was boiled for one hour with a solution of potassium dichromate (40 grams) and

sulphuric acid (36 c.c.) in water (520 c.c.). The acid so produced was purified by solution in dilute ammonia. On reprecipitation with dilute sulphuric acid, a yellow oil was obtained, which slowly solidified to a colourless solid, m. p. 289° [Found: N = 11.16; equivalent = 189.4. $C_{12}H_5O_6N_3(CO_2H)_2$ requires N = 11.16 per cent.; equivalent = 188.5].

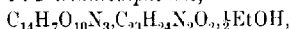
Attempts to characterise the acid by means of methyl and ethyl esters, its chloride, and its amide led in each case to oily products.

The orientation of the acid was proved by its further nitration with fuming nitric acid (5 parts) and sulphuric acid (6 parts) for twelve hours at 100° . The 4:6:4':6'-tetranitrodiphenic acid, m. p. 284° , so produced was further identified by its equivalent (214.3), and ethyl ester, m. p. 123° , and direct comparison of the acid and ester with those previously described.

Resolution of 1:4:6:4'-Trinitrodiphenic Acid.—By fractional crystallisation of the brucine salt of the racemic acid from water, the less soluble salt was obtained in a state of purity without much difficulty, but the more soluble salt was less easy to purify, and this was not pursued further when it was found that the quinidine salts (prepared from quinidine, of which $[\alpha]_D^{25} = +253.0^{\circ}$ for a 2 per cent. absolute alcoholic solution) were more suitable for the purpose.

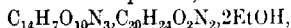
Brucine 1:4:6:4'-trinitrodiphenate consists of colourless, flat plates with rounded edges, m. p. 239 – 240° (decomp.), of which one part is soluble in about 1700 parts of cold water. For a 1 per cent. solution in 10N-acetic acid, $[\alpha]_D = -20.79^{\circ}$ (Found: $H_2O = 2.32$. $C_{60}H_{30}O_{18}N_7 \cdot 1\frac{1}{2}H_2O$ requires $H_2O = 2.28$ per cent. Found: for the anhydrous material dried at 130° , N = 8.56. $C_{60}H_{30}O_{18}N_7$ requires N = 8.41 per cent.).

Quinidine 1:4:6:4'-trinitrodiphenate,



separates from absolute alcohol in clusters of hexagonal prisms, frequently truncated, m. p. 229° (decomp.). For a 0.71 per cent. solution in chloroform, $[\alpha]_D^{25} = -191.1^{\circ}$ (Found: EtOH = 2.43. $C_{34}H_{31}O_{12}N_5 \cdot \frac{1}{2}EtOH$ requires EtOH = 2.20 per cent. Found: for the material dried at 130° , N = 9.81. $C_{34}H_{31}O_{12}N_5$ requires N = 9.57 per cent.).

Quinidine 1:4:6:4'-trinitrodiphenate,



crystallises from absolute alcohol in stout, rhombic prisms, m. p. 176° (decomp.). For a 0.71 per cent. solution in chloroform, $[\alpha]_D^{25} = +56.04^{\circ}$ (Found: EtOH = 8.55. $C_{31}H_{31}O_{12}N_5 \cdot 2EtOH$ requires EtOH = 8.24 per cent. Found: for the material dried at 130° , N = 9.51. $C_{34}H_{31}O_{12}N_5$ requires N = 9.57 per cent.).

d-4 : 6 : 4'-*Trinitrodiphenic acid*, $C_{12}H_5O_6N_3(CO_2H)_2$, prepared from the brucine salt as described in the cases of the active tetra-nitro-acids, was a yellow oil, which solidified after several weeks to minute prisms, m. p. $281-282^\circ$ (decomp.). For a 1.50 per cent. aqueous solution of the sodium salt, $[\alpha]_D^{25} = +156.8^\circ$. A somewhat less pure sample of the acid was titrated [Found: equivalent = 189.5. $C_{12}H_5O_6N_3(CO_2H)_2$ requires equivalent = 188.5]. For a preparation from the quinidine salt, a 1.27 per cent. aqueous solution of the sodium salt showed $[\alpha]_D^{25} = +143.1^\circ$.

l-4 : 6 : 4'-*Trinitrodiphenic acid*, $C_{12}H_5O_6N_3(CO_2H)_2$, from the quinidine salt, remained in the oily condition for several weeks, and had not solidified at the time of writing this paper. For a 0.49 per cent. aqueous solution of the sodium salt, $[\alpha]_D^{25} = -130.5^\circ$.

One of us (G. H. C.) expresses grateful acknowledgment of a grant from the Department of Scientific and Industrial Research which has enabled him to participate in this work. Further, we wish to thank Dr. P. C. Austin for the gift of some phenanthraquinone, and the Research Fund Committee of the Chemical Society for a grant towards the expenses of this investigation.

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[Received, February 22nd, 1923.]

XCII.—*Heteromorphism of Calcium Carbonate.* *Marble, Synthetic and Metamorphic.*

By MAURICE COPISAROW.

CALCIUM carbonate occurs in nature in a multitude of forms, which represent practically all transition stages between the crystalline and the amorphous state. Whilst generally calcium carbonate occurs in the anhydrous condition, hydrated forms are also known, namely, $CaCO_3 \cdot 5H_2O$, termed *hydrocalcite* in this paper (Salm-Horstmar, *Pogg. Ann.*, 1835, **35**, 515; Scheerer, *ibid.*, 1846, **68**, 382; Rammelsberg, *Ber.*, 1871, **4**, 569; Pfeiffer, *Arch. Pharm.*, 1879, [iii], **15**, 212), and $CaCO_3 \cdot 3H_2O$, which may be regarded as sub-hydrocalcite (Iwanoff, *Z. Kryst. Min.*, 1908, **44**, 87).*

The investigations of Rose (*Pogg. Ann.*, 1837, **42**, 354; 1838, **43**, 43), Vater (*Z. Kryst. Min.*, 1893, **21**, 433; 1895, **24**, 366; 1899,

* Ktycite (Laeroix, *Compt. rend.*, 1898, **128**, 602) and conchite (Kelly, *Sitzungsber. Bayr. Akad. München*, 1900, **30**, 187; *Jena Z. Naturw.*, 1901, **35**, 429) can scarcely be regarded as polymorphic forms distinct from calcite and aragonite (Vater, *Z. Kryst. Min.*, 1901, **35**, 166; Brauns, *N.J. Zentralb.*, 1901, 134).

30, 295), Adler (*Z. angew. Chem.*, 1897, 431), Stocks (*J. Soc. Chem. Ind.*, 1902, 21, 527), and Meigen (*Jahrb. Min.*, 1903, 11, 19; *Ber. Naturf. Ges. Freiburg*, 1903, 13, 40) showed that the separation of calcium carbonate in the form of precipitated chalk, calcite, and aragonite depends on (1) concentration of solution, (2) temperature, (3) velocity of separation, and (4) solvent medium.

The formation of hydrocalcite and probably of sub-hydrocalcite is conditioned by similar experimental factors (Becquerel, *Ann. Chim. Phys.*, 1833, 47, 9; Pelouze, *ibid.*, 1833, 48, 301; *Compt. rend.*, 1865, 60, 429; Koth, *Pogg. Ann.*, 1855, 95, 172; *J. pr. Chem.*, 1855, 65, 253; Hunt, *Amer. J. Sci.*, 1866, [ii], 42, 49; Bondomeau, *Bull. Soc. chim.*, 1875, [ii], 23, 100).

In respect to these transformations the present investigation revealed the following facts:

I. The formation of hydrocalcite, calcite, aragonite, and precipitated chalk by the double decomposition of alkali carbonates and soluble calcium salts is accomplished in stages—diffusion, solution, gelatinous form, and solid. The final form of the solid depends on the general experimental conditions.

II. The gelatinous phase obviated by slow diffusion may, under favourable conditions, be prolonged practically indefinitely.

This gelatinous form of calcium carbonate, which exists in an aqueous medium, although not without certain features in common with colloidal calcium carbonate prepared in methyl alcohol (Neuberg and Rewald, *Biochem. Z.*, 1908, 9, 545; *Z. Chem. Ind. Kolloide*, 1908, 2, 354), has certainly a shorter range of existence, and can be less definitely characterised than the latter.

On the basis of experiments described below, the gelatinous form of calcium carbonate may be regarded as unorientated molecular aggregates of hydrocalcite ($\text{CaCO}_3 \cdot 5\text{H}_2\text{O}$) formed in the course of a forced transformation of the initial liquid magma into hydrocalcite.

III. The effect of pressure, other conditions being equal, was found to result in the formation of crystalline instead of amorphous forms of calcium carbonate. Other aspects of the influence of pressure will be discussed at a later stage.

IV. In the study of the interaction of soluble calcium salts and alkali carbonates no indication of the formation of double salts of the type of halite and gay-lussite was found.

In the course of this work a new synthesis of marble was evolved which gives a new aspect to the metamorphosis of this substance, an aspect not only distinct from, but also opposed to, the existing igneous theory of its geological formation. Marble was first prepared synthetically by Hall (*Trans. Roy. Soc. Edinburgh*, 1801—

1806) by uncontrolled furnace heating of precipitated chalk or powdered limestone in a securely closed gunbarrel (see also Bucholz, *Neues allgemein. J. Chem.*, 1803, **1**, 271). These results, which were substantiated by Rose and Siemens (*J. pr. Chem.*, 1863, **88**, 256), Becker (*Min. petr.*, 1885, [ii], 7, 122) was unable to repeat. Data now available show that the experimental conditions of Hall's synthesis of marble were drastic in the extreme, Le Chatelier (*Compt. rend.*, 1892, **115**, 817) and Joannis (*ibid.*, p. 934) having found that the fusion point of calcium carbonate in a closed steel bomb lies just below that of gold at a pressure of 1000 kilos. per square centimetre. Boeke (*Z. anorg. Chem.*, 1906, **50**, 244) found no indication of fusion on heating calcium carbonate at 1400° under a pressure of 30 atmospheres of carbon dioxide. Only partial dissociation, and partial conversion to a marble-like substance, could be observed.

This transformation of calcium carbonate into marble led to the igneous theory of the geological formation of the latter, according to which the metamorphosis resulting in the production of marble is regarded as having been brought about by the incursion of molten granite and other analogous igneous rocks into beds of limestone, the heat and pressure so provided converting the latter into marble. The assumption, on the basis of Hall's work (*loc. cit.*), of a very high temperature and comparatively low pressure (22–30 atmospheres), as the representation of characteristic conditions of the geological formation of marble, is open to the following objections:

I. The condition of temperature and pressure cannot be regarded as a decisive criterion, for at high pressure and low temperature (Spring, *Bull. Akad. roy. Belg.*, 1895, [iii], **30**, 320; Becker, Hertzog, Jancke, and Polanyi, *Z. Physik*, 1921, **5**, 61), even more readily at moderately high temperature (Adams and Nicolson, *Proc. Roy. Soc.*, 1900, **67**, 228), and especially at moderate temperature and pressure (this communication), limestone shows a definite tendency to be transformed into marble.

II. Hall's synthesis of marble was carried out in the absence of other substances, which is a radically unnatural process. This contrast acquires a special significance in the light of the work of Rose (*Pogg. Ann.*, 1860, **111**, 156), Bourgeois (*Compt. rend.*, 1882, **94**, 991; *Bull. Soc. Min.*, 1883, **5**, 111), and Meigen (*Ber. Naturf. Ges. Freiburg*, 1902, **13**, 40) on the influence of fusible or soluble salts on the crystallisation of calcium carbonate.

The igneous theory likewise does not seem to be in accord with certain important geological facts, thus:

1. As a rule, granite and other igneous rocks do not, as might be expected on the basis of the theory, accompany marble, and in

the few cases where the two do occur in conjunction it is found, not that the igneous rock has penetrated the marble, but that the latter has filled the cavities and veins of the rock. This suggests that the mineral is of later formation than the rock, and that the calcium carbonate fills the cavities of the solid rock by sedimentation.

II. The transformation of limestone beds (to a large degree of fossil origin—diatoms, shells, corals, etc.) into marble under certain definite conditions, and the presence of organic matter even in the purest natural marble (8 parts per 100,000 parts of Carrara marble; Pollacci, *Gazzetta*, 1901, 32, i, 33) suggest that the marble was formed at a later period than the igneous rocks which occasionally accompany it. These facts also seem to indicate that the temperature of transformation of the various forms of calcium carbonate is much below that implied by either the igneous theory or Hall's synthesis of marble.

It is, of course, not impossible to find in proximity to marble and limestone igneous rocks of more modern formation. This would not, however, necessarily prove the general validity of the igneous theory. On the contrary, the partial conversion of limestone into deformed marble by the differential pressure of the molten lava would seem to be a good argument against the theory.

In the course of this work certain facts of intrinsic interest were elucidated.

I. The influence of pressure extends beyond facilitating crystallisation, in so far as it effects agglomeration of single crystals into compact masses, which may exhibit considerable cohesion.

Thus the additional effect of suitable pressure exerted in conjunction with conditions favourable to the formation of calcite, results in the formation of marble.

II. A substance which is chemically identical with natural marble of good quality and closely resembles it in physical properties is produced by (a) double decomposition of alkali carbonate and a soluble calcium salt at moderate temperature and pressure, and (b) heating powdered limestone or precipitated chalk with a concentrated solution of sodium chloride in an atmosphere of carbon dioxide under pressure.

These facts give a new aspect to the metamorphic transformation of calcium carbonate into marble.

Solution seems to be a characteristic feature of all these transformations, combination of favourable conditions of crystallising medium, solvent concentration, temperature, and pressure, leading to the formation of marble.

The new synthesis and the general geological study of marble would seem to exclude the igneous theory of its formation and

leave us with two possibilities as conceptions of the metamorphosis of marble, namely (a) sedimentation and (b) folding of rocks.

Examination of the available facts leads to the view that the two possibilities are supplementary rather than alternative, and with certain qualifications both may be taken as joint agents in the production of the conditions necessary for the formation in question.

Some of these qualifying conditions may be as follow :

I. In the case of the sedimentation process, the metamorphosis would occur only in strata which, originally or after a period of time, lay at a depth where a sufficiently high pressure and temperature were attained. In the upper regions, beds of limestone would be produced.

II. In the folding of rocks, the movement had to be such as to yield conditions of temperature and pressure, not only sufficient in magnitude, but also uniform in distribution. Differential conditions would result in a disruption or contortion of the mineral due to the twisting and twinning of the crystalline structure. That the movement of terrestrial rocks is not always regular, and the exerting pressure uniform, is shown by the occasional occurrence of deformed marble; the possibility is, however, not excluded of the deformation having been caused by the incursion of lava at some later period (compare the conception of marmarosis; Geikie, "Text-book of Geology," 1882).

Dealing with the mechanism of the formation of marble, it will be observed that, in both methods described below, there is a common feature, namely, a temporary state of solution preceding the separation of the solid form: also that the conditions of formation of marble are practically those of calcite with the additional effect of pressure.

The influence of carbon dioxide and brine on the solubility of calcium carbonate may be seen from the following table :

Solubility (mg. per litre) of calcium carbonate (powdered limestone).

Temperature.	Distilled water.	Water saturated with	
		CO ₂ at 1 atmos.	Sea-water.
18°	—	—	191
25	14.33	1100-1300	—
50	15.04	—	—
100	17.19	—	—

(Compare Salisbury Dana, "Descriptive Mineralogy," London, 1892; Rosenbusch, "Physiographie," Stuttgart, 1905; Linck, "Grundr. der Krystallographie," Jena, 1920; Niggli, "Lehrbuch der Mineralogie," Berlin, 1920.)

In the case of the sodium carbonate \rightleftharpoons calcium chloride double decomposition, the separation of calcium carbonate is not quantitative, some remaining dissolved in the saline medium (Berzelius,

Jahresber., 1844, **23**, 106; Bewad, *J. Russ. Phys. Chem. Soc.*, 1885, I, 89). Such solubility may be perhaps due to the formation of double salts of the type $\text{CaCO}_3 \cdot \text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{CaCO}_3 \cdot \text{Na}_2\text{CO}_3 \cdot 5\text{H}_2\text{O}$, although no indication of their presence could be found. The separation of calcium carbonate is still more retarded in presence of ammonium carbonate (Fresenius, *Z. anal. Chem.*, 1863, **2**, 49).

The formation of pearl and of mother-of-pearl is closely connected with the heteromorphism of calcium carbonate. Apparently the deposition takes place at the transition temperatures of hydrocalcite and the anhydrous forms of calcium carbonate (hence the importance of latitude, sea-depth, and oceanic currents). This slow deposition of calcium carbonate, a result of exudation, is akin in certain respects to the formation of stalactite and egg-shell and results in the environment of organic, chiefly protein, matter in the formation of a compact mass, consisting of a multitude of thin nacreous layers of calcium carbonate. This conception is fully substantiated by the work of Clément and Rivière (*Compt. rend.*, 1922, **174**, 1353) on nacreous surfaces. The underlying causes and general features of this gradual lamellar deposition seem strikingly connected with the periodicity of the Liesegang phenomenon.

EXPERIMENTAL.

Neuberg and Rewald (*Biochem. Z.*, 1908, **9**, 545; *Z. Chem. Ind. Kolloide*, 1908, **2**, 354) found that in organic solvents, especially methyl alcohol, calcium carbonate could exist in the colloidal state practically for an indefinite period. Rose (*Pogg. Ann.*, 1837, **42**, 354) observed an intermediate "jelly" state in the preparation of precipitated chalk by the double decomposition of alkali carbonates and soluble calcium salts.

To investigate the nature of this gelatinous mass and the conditions of transformation of the various forms of calcium carbonate, the following experiments were carried out.

Hydrocalcite.

Series I.—Ten per cent. aqueous solutions of sodium carbonate and calcium chloride were mixed in equimolecular proportions at 21° and stirred for a moment in a glass beaker. The mixture formed a perfectly clear solution, which could, by rapid manipulation, be filtered without residue through a Büchner funnel. On standing, the solution gradually became opalescent, then turbid, and finally thickened, setting in the course of two minutes to a jelly-like mass, slightly soapy to the touch. After a time, the gelatinous mass broke up into a fine powder, which gradually settled as precipitated chalk. The primary solution and the gelatinous

calcium carbonate, although invariably formed, have but a temporary existence above 18° , which is briefer the higher are the temperature and the concentration, and the more vigorous is the agitation of the mixture, which may be regarded as a very unstable supersaturated solution of calcium carbonate.

Series II.—The solutions of sodium carbonate and calcium chloride were mixed at $5-6^{\circ}$. Again the solution gradually became viscous, and opaque when viewed in bulk. Examination of this gelatinous magma in layers $\frac{1}{2}$ to 1 cm. in thickness showed it to be distinctly translucent, the mass consisting of large, non-crystalline flocks, which did not lend themselves to filtration. This state is conditioned distinctly by the temperature and will persist almost indefinitely at 5° to 12° . Rise of temperature above 15° induced gradual breaking up of this gelatinous mass, with the formation of precipitated chalk. On stirring the gelatinous magma at a temperature within its range of stability, the flocks were disrupted, liberating some of the occluded liquid without the solid showing signs of settling down. Examined with a magnifying glass, the resultant mass was found to be unaltered, consisting of very small, non-crystalline, less translucent particles. This mass was filtered through a Büchner funnel specially made for the purpose.*

The gently pressed residue in the Büchner funnel was white, opaque, amorphous, and voluminous, and much lighter than precipitated chalk (Found : $\text{CaCO}_3 = 49.9$; $\text{NaCl} = 3.1$; $\text{H}_2\text{O} = 47.0$. $\text{CaCO}_3, 5\text{H}_2\text{O}$ requires $\text{CaCO}_3 = 52.63$; $\text{H}_2\text{O} = 47.37$ per cent.).

The substance showed no alteration on cooling to -10° . On allowing it to gain the room temperature, the mass became dough-like and then separated into a white, finely divided precipitated chalk and brine. On keeping the substance in an evacuated desiccator over either calcium chloride, concentrated sulphuric acid, phosphoric anhydride, or sodium sulphate, the desiccator being immersed in a bath kept at $5-7^{\circ}$, the substance rapidly shrank without becoming "dough-like," forming a fine powder (chalk). The same change took place, although not so rapidly, on keeping the substance in a desiccator connected with a suction pump in the absence of any dehydrating agent.

Series III.—When solutions of sodium carbonate and calcium chloride cooled to 1° were mixed, the early stages of the reaction were similar to those described in Series II. The solution became opalescent after a couple of minutes' standing, the mass becoming

* The funnel was made of tinned iron, rather deeper than the usual Büchner funnel, the perforated bottom being about 9 cm. in diameter. The funnel was fitted with an outer jacket of the same material, whereby the temperature could be kept at $4-5^{\circ}$ during the whole filtration.

gelatinous, but this gelatinous magma had no longer the permanent character observed in the previous case. On keeping for four hours at $1-2^{\circ}$, the flocculent mass was gradually transformed into a voluminous mass of minute, feathery crystals, reflecting light. The transformation from the gelatinous to the crystalline state was attained by cooling the gelatinous magma obtained in Series II. The crystalline mass was filtered and gently pressed, the temperature being maintained at $1-2^{\circ}$ (Found: $\text{CaCO}_3 = 51.5$; $\text{NaCl} = 1.3$; $\text{H}_2\text{O} = 47.2$. $\text{CaCO}_3 \cdot 5\text{H}_2\text{O}$ requires $\text{CaCO}_3 = 52.63$; $\text{H}_2\text{O} = 47.37$ per cent.).

No change was observed on cooling the crystalline product to -20° . On raising the temperature above 18° , or on drying, the substance underwent changes similar to those described in Series II. The products from Series II and III, when free from sodium chloride, are tasteless, and do not give the Meigen's reaction with cobalt nitrate (*Centralblatt*, 1901, II, 1128; Wyruboff, *Bull. Soc. franç. Min.*, 1902, 25, 69). The product from Series III both in composition and properties is identical with the substance, $\text{CaCO}_3 \cdot 5\text{H}_2\text{O}$, found naturally and also prepared synthetically. No crystalline modification having the composition $\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$, recorded by Pelouze (*Compt. rend.*, 1863, 60, 429), could be detected. It must be noted that in the determination of the composition of the substance, one is faced with two divergent difficulties: (a) at higher temperatures and on prolonged draining, low results were obtained owing to dehydration, and (b) at low temperatures and with a short period of draining, high values resulted owing to the difficulty of freeing the crystals of the adventitious water. The crystalline substance, $\text{CaCO}_3 \cdot 5\text{H}_2\text{O}$, closely resembling calcite in chemical properties, and similar to the calcite and the aragonite produced by the agency of heat, may be termed *hydrocalcite*.

The crystalline substance, $\text{CaCO}_3 \cdot 3\text{H}_2\text{O}$, described by Iwanoff (*loc. cit.*) and Pelouze (*loc. cit.*), which may be synthetically prepared by partial dehydration of hydrocalcite, and which is similar to the latter (Meigen's reaction), may be termed *subhydrocalcite*.

Slow Diffusion.

From the experiments described above, it was evident that, at all stages of its transformation, the calcium carbonate was greatly hampered in its normal development by the considerable momentary concentration of its molecules in the aqueous sodium chloride medium at any given period. This resulted in inhibition of molecular orientation and consequent crystalline deformity. Conditions were required where practically an unlimited number of calcium carbonate molecules formed *in situ* (by double decomposi-

tion) gradually and unhindered move and orientate in the aqueous salt medium.

These conditions were satisfactorily attained, especially at low and moderate temperatures, in the following manner:

Series IV.—Solutions of sodium carbonate (7–10 per cent.) were allowed to run gently down the side of the beaker on to 40–50 per cent. solutions of calcium chloride, taken in excess. The temperatures of the solutions were definite and constant. Owing to the considerable difference of density, the solutions formed two layers, separated at low temperatures by a thin layer of gelatinous calcium carbonate, which served as a diffusion membrane.

The diffusion was found to proceed mainly upwards, the calcium carbonate being enveloped by a solution of sodium chloride in a sodium carbonate medium. On carrying out the experiment at 5° and allowing the diffusion to proceed at this temperature for twenty-four hours, the upper layer, and partly the lower, was found to be filled with a thick growth of well-developed crystals, fairly long, pyramidally pointed prisms. The saline medium was siphoned off, and the crystals drained and gently pressed on a Büchner funnel kept at 5° (Found: $\text{CaCO}_3 = 49.7$; $\text{NaCl} = 3.2$; $\text{H}_2\text{O} = 47.1$. $\text{CaCO}_3 \cdot 5\text{H}_2\text{O}$ requires $\text{CaCO}_3 = 52.63$; $\text{H}_2\text{O} = 47.37$ per cent.).

The substance is identical with the product obtained by Bon-donneau (*loc. cit.*) and with the product isolated in Series III, but owing to the difference in the size of the crystals it occludes a larger quantity of sodium chloride. With rise of temperature, the crystals became opaque (17–18°) and then decrepitated, yielding chalk and water.

Calcite and Aragonite.

On carrying out the experiments at temperatures ranging from 20° to 36°, the diffusion resulted in the formation of a less voluminous, crystalline product, containing no water of crystallisation and giving no reaction with cobalt nitrate (Meigen's reaction), and found to be identical with calcite. Experiments carried out at higher temperatures (40° and upwards) gave crystalline products, which, judging by the gradual increase of (1) their reactivity with cobalt nitrate, and (2) their density, were mixtures of calcite and aragonite, the proportion of calcite diminishing with rise of temperature. However, no aragonite, free from other forms of calcium carbonate, could be prepared. This is really not surprising, as the transition point of aragonite \rightarrow calcite is influenced not only by the time factor, but also by media and temperatures specific for each medium and concentration (Rose, *loc. cit.*; Bourgeois, *Compt. rend.*, 1886, 103, 1088; Knofer, *Wied. Ann.*, 1889, 38, 136; Watson, *Chem.*

News, 1891, 68, 109; Adler, *Z. angew. Chem.*, 1897, 431; Meigen, *Jahrb. Min.*, 1903, 2, 19; Cornu, *Oesterr. Z. Berg. Huttenw.*, 1907, 55, 598; Barlow and Pope, *T.*, 1908, 93, 1528).

The difficulty of controlling the formation of pure forms of calcium carbonate at high temperatures is greatly increased by the rapid currents which, disturbing diffusion, produce ultimately precipitated chalk. The conditions of transformation of calcite \rightarrow aragonite having already been studied in detail by many workers (see references above), no further investigation of this problem was deemed necessary.

Calcite and Limestone.

Influence of Pressure. Series V.—Owing to the impracticability of employing solutions for the production of calcium carbonate under pressure, the following method was adopted.

A wrought-iron, thick-walled tube (12×2.5 cm. internal bore), closed at one end and fitted with a steel piston (with a lead washer), was filled with finely powdered anhydrous calcium chloride and sodium carbonate decahydrate in equimolecular proportions. The sodium carbonate was packed as the top layer. The tube was placed in a powerful hand-press, with the screw on the piston. The pressure was gradually increased, reaching its maximum in the course of six hours, this pressure being maintained for twelve hours. On releasing the pressure, the reaction mixture was found to consist of a coarse, granular powder and a solution. The powder was washed with cold water, dried, and found to be identical with calcite in the form of small, hard, crystalline granules. Calcite in a finer state of division was obtained on reversing the order of the layers, or better, employing an intimate mixture of the two salts taking part in the reaction. Pressure, exerted rapidly by hammering the piston instead of being gradually increased by means of the press, resulted in a product resembling powdered limestone. In no case could cohesion be observed.

Influence of Heat. Series VI.—A cylindrically-shaped, narrow copper vessel was packed with finely powdered anhydrous calcium chloride and hydrated sodium carbonate. The proportions and the mode of packing were identical with those employed in Series V. The vessel was kept in an oil-bath at 210° for six hours. The hard product was cooled, broken up into large pieces, thoroughly washed with running cold water, drained, and dried. It then consisted of a hard, somewhat porous, granular, non-crystalline substance, resembling limestone in appearance and cohesion. When the conditions of mixing were modified as in series V, the product was found to be more porous, and consequently more brittle.

The object of the experiments described in Series V and VI was

to study the effect of pressure and heat, taken separately, on the crystallisation and the cohesion of calcium carbonate; the experiments have no direct bearing on the formation of either calcite or limestone in nature.

Marble.

In view of the facts that (a) saline media and carbon dioxide represent solvents for calcium carbonate, (b) pressure conditions crystallisation, with a special tendency to the formation of calcite, and (c) high temperature facilitates formation of massive material, it was thought that a combination of all three conditions would result in the formation of marble. This expectation was subsequently fully substantiated. Two methods of formation of marble were evolved, both of which, although quite distinct from one another, yet incorporate all the conditions set forth above.

The first method, a direct process of formation of marble by double decomposition, may be characterised as that of chemical synthesis; the second—an indirect process—is perhaps the nearest approach to the metamorphic formation of marble (marmarosís).

Series VII.—Powdered anhydrous calcium chloride and hydrated sodium carbonate were packed in two layers, the latter substance forming the top layer, in an autoclave, heated in an oil-bath. The internal temperature was raised to 300° in the course of two hours and kept at 300–305° for eight hours, the pressure rising to 24 atmospheres. The autoclave was then allowed to cool. The top layer, a saturated solution of sodium chloride mixed with undissolved sodium chloride and some unchanged material or calcium carbonate, was poured off. The bottom layer was found to be a compact, stone-like solid. It was broken up into fairly large pieces, well washed with cold water, and allowed to drain and dry. The product was found to resemble the purest natural marble: saccharoidal in structure, its fracture surface had a sparkling appearance, owing to the refraction of light by the crystalline facets, revealed by the cleavage. The powdered product gave no Meigen's reaction with cobalt nitrate (calcite). Although apparently non-porous, the product occasionally exhibited small cavities, when examined in cross-section. The substance acquired a magnificent polished surface when cut, filed, rubbed on sand and emery-papers, and finished off on rotating, oiled cloth and velvet pads.

Similar products were obtained by employing hydrated calcium chloride and anhydrous sodium carbonate, or by using both salts in the hydrated condition—the order of layers being preserved. On reversing the order of packing, or using an intimate mixture of the salts, the product was found to be somewhat more porous.

Marble of good quality was obtained when sodium bicarbonate

was used in place of sodium carbonate. In this case, hydrated calcium chloride was employed, and the pressure in the autoclave released on cooling to 100° . On carrying out the experiment at $205\text{--}210^{\circ}$, the product was found to be of smaller cohesion.

Series VIII.—Precipitated chalk was mixed with a saturated solution of sodium chloride, to form an easily stirrable paste, in an open autoclave. The mixture was saturated with carbon dioxide at room temperature, the autoclave was then sealed and heated in an oil-bath. The internal temperature was raised to 300° in the course of two hours, the pressure reaching 27 atmospheres. After eight hours' heating at $300\text{--}305^{\circ}$, the autoclave was allowed to cool. The product was found to be identical in every respect with that described in Series VII. When finely-powdered limestone was used, the marble obtained showed a coloration due to the impurities contained in the starting material.

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[Received, August 22nd, 1922.]

XCIH.—*Heteromorphism of Calcium Sulphate. Alabaster and its Synthesis.*

By MAURICE COPISAROW.

CALCIUM sulphate occurs chiefly in conjunction with stratified rocks, but is occasionally met with in crystalline rocks. It is usually found associated with rock salt, calcium carbonate, and various silicates, the latter two of which influence its pseudomorphism (Lacroix, *Nouv. Arch. Museum, Paris*, 1897, 9, 201).

Calcium sulphate occurs in the following forms :—(I) $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, as gypsum and alabaster; (II) CaSO_4 , as anhydrite (ordinary and pseudomorphic); (III) $3\text{CaSO}_4 \cdot 5\text{H}_2\text{O}$, as a mineral found in Peru (*Verh. deutsch. Wiss. Ver. Santiago*, 1901, 10, 1); and (IV) $\text{CaSO}_4 \cdot \text{H}_2\text{O}$, as semihydrate, artificially prepared (van't Hoff and his collaborators, *Sitzungsber. Preuss. Akad. Wiss. Berlin; Extr. Arch. Néerland; Z. Elektrochem.; Z. physikal. Chem.; and Ber.*, 1900—1905).

The conversion of gypsum into anhydrite was studied by Mitscherlich, Hoppe-Seyler, Gorgeu, and especially by Rose (*Sitzungsber. Preuss. Akad. Wiss., Berlin*, 1871, 363), Vater (*ibid.*, 1900, 17, 269), and van't Hoff (*loc. cit.*). The transformation takes place under the influence of heat, this action being accelerated in presence of the chlorides of calcium and the alkali metals. Spezia (*Atti R. Acad. Sci. Torino*, 1886, 21, 912) has proved that no dehydration takes place by the action of pressure alone.

Under the influence of moisture, anhydrite is converted com-

pletely, although not so rapidly as semihydrate, into gypsum. Extensive beds of anhydrite are thus altered in part or throughout (Bex, Switzerland). The velocity of hydration, like that of dehydration, is influenced by the presence of other mineral salts (Rohland, *Z. Elektrochem.*, 1908, **14**, 421; Bell and Taber, *J. Physical Chem.*, 1908, **11**, 632, 637; van't Hoff, *loc. cit.*). The rate of hydration and the form of product depend on the original state of hydration. Anhydrite gives granular gypsum, whilst semihydrate leads to plaster of Paris (Schott, *Dingl.*, 1872, 202; Knapp, *ibid.*, p. 513; van't Hoff and Just, *Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1903, 249).

The results obtained by the author in the study of calcium carbonate (this vol., p. 785) were such as to make it desirable to investigate on similar lines the transformations of calcium sulphate. During these investigations the following observations were made:

(1) Neither a state of temporary supersaturation, nor the gelatinisation which is so characteristic a feature of the formation of calcium carbonate by double decomposition, could be observed in the production of calcium sulphate.

This contrast seems to be due to the fact that calcium sulphate shows no tendency to form varieties of greater hydration than that of gypsum. No colloidal calcium sulphate as prepared in alcoholic solution by Neuberg and Rewald (*Biochem. Z.*, 1908, **9**, 541; *Z. Chem. Ind. Koll.*, 1908, **2**, 354) could be observed in aqueous medium.

(2) Owing to the absence of the gelatinous membrane, the slow diffusion, so well defined in the case of calcium carbonate, did not develop satisfactorily, the whole reaction being completed within a few minutes with the formation of a product somewhat coarser than the usual impalpable precipitate.

(3) Double decomposition (sodium sulphate and calcium chloride) under pressure resulted in the formation of gypsum in the form of coarsely granular particles.

(4) Double decomposition at high temperature led to the formation of finely-granular, compact anhydrite.

(5) Double decomposition at high temperature and pressure resulted in the formation of an alabaster-like substance of considerable cohesion. It was found to be easily polishable, and on fracture revealed a finely-grained structure, the facets reflecting light. This double decomposition was carried out with either (a) hydrated sodium sulphate and anhydrous calcium chloride, (b) anhydrous sodium sulphate and hydrated calcium chloride, or (c) hydrated sodium sulphate and calcium chloride.

Method (a) gave the most satisfactory result, yielding a product of maximum compactness.

The mechanism of the formation of alabaster* is essentially similar to that of marble. We may assume a momentary state of solution, pressure operating in addition to conditions which would ordinarily result in the formation of semihydrate or anhydrite.

The study of the geological formation of gypsum, anhydrite, and alabaster shows this synthesis of alabaster to be a close approximation to the natural process in so far as conditions are concerned. The actual reagents taking part in the metamorphosis have perhaps varied with the locality.

EXPERIMENTAL.

Series I.—Solutions of sodium sulphate and calcium chloride in equimolecular proportions were mixed together at 20° . The reaction showed no transition stages, the calcium sulphate (gypsum) coming down as an impalpable powder. Concentration of the solutions had but little effect on the state of division of the product. At higher temperatures, a less finely divided product was obtained.

Series II.—Dilute solutions (5—7 per cent.) of sodium sulphate were carefully poured on concentrated solutions (40—50 per cent.) of calcium chloride, in the same manner as that employed in the case of calcium carbonate. Experiments were carried out at temperatures ranging from 0° to 55° . No slow diffusion, or variation in the state of hydration of the product with temperature, made itself manifest in these instances. The only variations observed were the velocity of reaction and state of division of the gypsum, both of which increased with rise in temperature. The product obtained at 15° was finely granular and readily separable by filtration.

Series III.—Finely powdered, hydrated sodium sulphate and anhydrous calcium chloride were placed in a wrought-iron tube and subjected to pressure. The order of packing and the manipulation were the same as those adopted in the case of calcium carbonate. The maximum pressure attained in the course of six hours was maintained for twelve hours. The viscous paste obtained was treated with running cold water, filtered, and dried at room temperature and ordinary pressure, yielding a coarse, crystallogranular gypsum (on analysis— $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), bright in appearance and showing a tendency to reflect light.

Series IV.—A narrow copper vessel was packed with powdered, anhydrous calcium chloride and hydrated sodium sulphate, the

* Modern alabaster ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) is chemically quite distinct from the "alabaster" of Theophrastus and Pliny, which was mainly or wholly stalagmite (CaCO_3). Hence the latter is still occasionally referred to as "oriental alabaster."

latter forming the top layer, and heated in an oil-bath for eight hours at 205--210° (temperature of melting). The analysis of the cooled compact mass showed it to contain no water, thus proving that the dehydration of calcium sulphate in presence of sodium chloride is complete under conditions which ordinarily produce only semihydrate (van't Hoff and others, *loc. cit.*).

On treating this mass, when cold, with running water for half an hour, the sodium chloride and any unchanged salts were readily dissolved, leaving the calcium sulphate in a finely grained, porous, somewhat brittle, anhydrous form. Similar results were obtained by carrying out the experiment at 300°.

Series V.—Equimolecular quantities of finely powdered, hydrated sodium sulphate and anhydrous calcium chloride were packed in an autoclave, the order of packing being as in Series IV. The autoclave was sealed and heated in an oil-bath, the internal temperature being raised to 300° in the course of two hours. The heating was continued for another six hours, the temperature being kept at 300--310°; the maximum pressure attained was 12.5 atmospheres. The cold product was found to consist of a hard, compact mass, covered with a thin paste of brine, solid sodium chloride, and any unreacted starting material. The hard solid was broken up into pieces about 1.5--2 cm. in cross section, washed well with cold water, drained, and allowed to dry in the air. The product was softer than marble; on fracture, it showed a finely crystallogranular structure and reflected light. Analysis of the finely powdered product indicated the composition $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, only traces of sodium chloride being found. In appearance, the substance closely resembled alabaster, and it readily gave a fine polished surface. A polished specimen kept in pure cotton-seed oil at 95° for half-an-hour and then polished again on rotating velvet pads, assumed a pretty, unctuous appearance.

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[Received, August, 22nd 1922.]

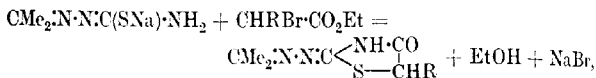
XCIV.—*Reactions of Thiosemicarbazones. Part II.* *Action of Esters of α -Halogenated Acids.*

By FORSYTH JAMES WILSON and ROBERT BURNS.

IN Part I (T., 1922, **121**, 870), an account of the reactions between the sodium derivative of acetone-thiosemicarbazone and certain halogen compounds was communicated. Esters of chloroacetic acid yielded a ψ -thichydantoin derivative of a new type,

$\text{CMe}_2\text{N}\cdot\text{N}\cdot\text{C} \begin{smallmatrix} \text{NH}\cdot\text{CO} \\ | \\ \text{S}-\text{CH}_2 \end{smallmatrix}$, 2:4-diketotetrahydrothiazole-2-isopropylidenhydrazone, hydrolysis of which with acid gave 2:4-diketotetrahydrothiazole by elimination of acetone and hydrazine. It was not found possible to remove acetone only and isolate the intermediate hydrazone; the cases reported in this communication have been more successful.

We have now investigated the reactions between the sodium derivative of acetone thiosemicarbazone and ethyl α -bromopropionate, ethyl α -bromo-*n*-butyrate, and ethyl phenylbromoacetate. With each of these esters the product was the 2-isopropylidenhydrazone derivative of a 2:4-diketotetrahydrothiazole, the reactions, which were carried out in boiling alcoholic solution, proceeding according to the scheme



the yields being from 70 to 75 per cent. of the theoretical.

Hydrolysis of these compounds by boiling with concentrated hydrochloric acid for several hours removed acetone and hydrazine and gave a 2:4-diketotetrahydrothiazole, $\text{CO} \begin{smallmatrix} \text{NH}\cdot\text{CO} \\ | \\ \text{S}-\text{CHR} \end{smallmatrix}$, in very satisfactory yield. If, however, the hydrolysis was effected by boiling with 2*N*-hydrochloric acid for about fifteen minutes, acetone only was removed and the intermediate hydrazone, $\text{NH}_2\cdot\text{N}\cdot\text{C} \begin{smallmatrix} \text{NH}\cdot\text{CO} \\ | \\ \text{S}-\text{CHR} \end{smallmatrix}$,

could be isolated as the hydrochloride. These two types of hydrolysis were quite sharply distinguished in the cases investigated. The hydrochlorides of these hydrazones, which, it is believed, represent a new type of ψ -thiohydantoin derivatives, can be obtained in good yield and are well-defined, crystalline salts which appear to be quite stable. In aqueous solution, they reacted readily with benzaldehyde, giving the benzyldene derivative, $\text{CHPh}\cdot\text{N}\cdot\text{N}\cdot\text{C} \begin{smallmatrix} \text{NH}\cdot\text{CO} \\ | \\ \text{S}-\text{CHR} \end{smallmatrix}$. Attempts were made to obtain the

free hydrazones from these hydrochlorides, but with unsatisfactory results owing to the unstable nature of the hydrazones. We succeeded, however, in preparing 2:4-diketo-5-ethyltetrahydrothiazole-2-hydrazone, $\text{NH}_2\cdot\text{N}\cdot\text{C} \begin{smallmatrix} \text{NH}\cdot\text{CO} \\ | \\ \text{S}-\text{CHEt} \end{smallmatrix}$, from its hydrochloride

by means of sodium carbonate as a crystalline powder which was moderately stable. All the compounds described were soluble in aqueous sodium hydroxide.

These hydrazones and the 2:4-diketotetrahydrothiazoles contain an asymmetric carbon atom, and it is hoped to effect a resolution and to bring about the synthesis of an optically active one. We also propose to investigate the interaction between thiosemicarbazones and esters of other classes of halogenated acids.

EXPERIMENTAL.

Reaction with Ethyl α -Bromopropionate. 2:4-Diketo-5-methyltetrahydrothiazole-2-isopropylidenehydrazone, $\text{CMe}_2\text{N}\cdot\text{N}\cdot\text{C} \begin{smallmatrix} \text{NH}\cdot\text{CO} \\ \diagdown \\ \text{S}-\text{CHMe} \end{smallmatrix}$ —

Acetonethiosemicarbazone, dissolved in boiling alcohol, was treated with sodium ethoxide (1 mol.) in alcohol, and ethyl α -bromopropionate (slightly more than 1 mol.) was added to the cooled solution, which was kept at room temperature for one hour and then boiled for half an hour under reflux. Sodium bromide was removed by filtering the boiling solution which, on cooling, deposited the tetrahydrothiazole derivative. This was recrystallised from alcohol, from which it separated in fine, white needles melting at 150° . It was slightly soluble in benzene, sparingly soluble in ether or water. The above method may be varied by dissolving the previously prepared sodium derivative of acetonethiosemicarbazone in alcohol, adding the ester, and then proceeding as before (Found: $\text{N} = 22.66$, 22.70 . $\text{C}_7\text{H}_{11}\text{ON}_3\text{S}$ requires $\text{N} = 22.70$ per cent.).

2:4-Diketo-5-methyltetrahydrothiazole, $\text{CO} \begin{smallmatrix} \text{NH}\cdot\text{CO} \\ \diagdown \\ \text{S}-\text{CHMe} \end{smallmatrix}$ —The

above isopropylidene derivative was boiled under reflux with concentrated hydrochloric acid for three hours and the solution then evaporated to dryness on the water-bath. The residue was extracted with hot benzene, and the undissolved solid identified as hydrazine hydrochloride by reduction of Fehling's solution and by conversion into benzalazine. The benzene solution on evaporation gave an oil which distilled at $165\text{--}168^\circ/20\text{ mm.}$; the distillate, on cooling with solid carbon dioxide and ether, solidified to a crystalline mass which melted at $46\text{--}47^\circ$. From its properties it is evidently the substance already described by Wheeler and Barnes (*Amer. Chem. J.*, 1900, **24**, 78), who prepared it by a different method (Found: $\text{N} = 10.64$. Calc., $\text{N} = 10.69$ per cent.).

2:4-Diketo-5-methyltetrahydrothiazole-2-hydrazone Hydrochloride, $\text{NH}_2\text{N}\cdot\text{C} \begin{smallmatrix} \text{NH}\cdot\text{CO} \\ \diagdown \\ \text{S}-\text{CHMe} \end{smallmatrix} \cdot \text{HCl}$.—The isopropylidene derivative was boiled with 2*N*-hydrochloric acid under reflux for about fifteen minutes and the solution, after filtration from a small quantity of insoluble matter, was evaporated to dryness under reduced pressure at $40\text{--}50^\circ$. Acetone was recognised in the distillate by

its odour and by the iodoform reaction. The residue, consisting of the hydrochloride, was a white, granular, crystalline substance which was slightly hygroscopic, very soluble in water, slightly soluble in alcohol, and practically insoluble in ether. It decomposed above 220° . The aqueous solution gave a precipitate of silver chloride with silver nitrate and nitric acid and it appeared to give a silver salt due probably to the tetrahydrothiazole complex, but this was not investigated. The substance reduced Fehling's solution on boiling (Found: $N = 22.99, 23.15$. $C_4H_7ON_3S \cdot HCl$ requires $N = 23.14$ per cent.). The *benzylidene* derivative was prepared by shaking an aqueous solution of the hydrochloride with benzaldehyde and recrystallising the product from alcohol, from which it was deposited as fine, white needles melting at 236° . It was slightly soluble in cold alcohol and in water (Found: $N = 18.03$. $C_{11}H_{11}ON_3S$ requires $N = 18.03$ per cent.).

It was not found possible to obtain the hydrazone itself in pure condition from its hydrochloride.

Reaction with Ethyl α -Bromo-n-butyrate. **2:4-Diketo-5-ethyltetrahydrothiazole-2-isopropylidenehydrazone**, $CMe_2N:N:C \begin{smallmatrix} < NH \cdot CO \\ S - CHEt \end{smallmatrix}$

This reaction was carried out in the same way as with ethyl α -bromopropionate. The compound was recrystallised from alcohol, from which it separated in fine, white, glistening needles melting at 116° . It was only slightly soluble in benzene, ether, or water (Found: $N = 20.99, 20.90$. $C_8H_{13}ON_3S$ requires $N = 21.11$ per cent.).

2:4-Diketo-5-ethyltetrahydrothiazole was prepared from the above isopropylidene derivative by boiling with concentrated hydrochloric acid as in the previous case. After recrystallisation from a mixture of benzene and light petroleum, it melted at $63-64^{\circ}$ and was easily soluble in alcohol or benzene, less soluble in light petroleum. It agreed in melting point and properties with the substance previously prepared by Wheeler and Barnes (*loc. cit.*, p. 76) by another method.

2:4-Diketo-5-ethyltetrahydrothiazole-2-hydrazone hydrochloride was prepared by boiling the isopropylidene derivative with 2*N*-hydrochloric acid as with the corresponding 5-methyl compound. It was a white, granular, crystalline solid, soluble in water, slightly soluble in alcohol, and practically insoluble in ether, and decomposed on heating at $215-220^{\circ}$ (Found: $N = 21.44, 21.39$. $C_5H_9ON_3S \cdot HCl$ requires $N = 21.49$ per cent.). The *benzylidene* derivative was prepared in the usual way. After recrystallisation from alcohol, it was obtained as white, microscopic needles melting at 206° and was practically insoluble in ether,

water, or cold alcohol (Found : N = 16.90. $C_{12}H_{13}ON_3S$ requires N = 17.00 per cent.).

2:4-Diketo-5-ethyltetrahydrothiazole-2-hydrazone was prepared from equivalent quantities of the hydrochloride and sodium carbonate in aqueous solution. After the effervescence had ceased, the solution was evaporated to dryness at room temperature in a vacuum over sulphuric acid, the residue was washed with a small quantity of cold water to remove sodium chloride, and analysed after drying in a vacuum (Found : N = 26.23. $C_5H_9ON_3S$ requires N = 26.41 per cent.). It was a white, crystalline powder, soluble in hot alcohol, slightly soluble in benzene, ether, or water. It melted at 139° and appeared to be moderately stable, becoming slightly yellow on keeping.

Reaction with Ethyl Phenylbromacetate. 2:4-Diketo-5-phenyltetrahydrothiazole-2-isopropylidenehydrazone, $CMc_2:N:N'C<\begin{smallmatrix} NH\cdot CO \\ S-CHPh' \end{smallmatrix}$

was prepared by the usual method from this ester and the sodium derivative of acetone-thiosemicarbazone. Recrystallisation from alcohol gave fine, white needles melting at $198-199^\circ$ which were not appreciably soluble in benzene, ether, or water (Found : N = 16.89, 16.96. $C_{12}H_{13}ON_3S$ requires N = 17.00 per cent.).

2:4-Diketo-5-phenyltetrahydrothiazole was obtained by hydrolysis of the previous compound by means of concentrated hydrochloric acid in the usual way. After recrystallisation from alcohol, it melted at $125-126^\circ$ and corresponded in its properties with the compound prepared according to another method by Wheeler (*Amer. Chem. J.*, 1901, **26**, 352).

2:4-Diketo-5-phenyltetrahydrothiazole-2-hydrazone hydrochloride, prepared from the isopropylidene-hydrazone by hydrolysis with dilute hydrochloric acid in the usual way, was a white, micro-crystalline powder which decomposed above 240° ; it was rather sparingly soluble in cold water, soluble with difficulty in alcohol, and practically insoluble in ether (Found : N = 17.20, 17.15. $C_9H_9ON_3S\cdot HCl$ requires N = 17.25 per cent.). The benzylidene derivative, prepared in the usual way and recrystallised from alcohol, formed microscopic, white, hair-like crystals melting at 257° ; it was only slightly soluble in cold alcohol, benzene, ether, or water (Found : N = 14.15. $C_{16}H_{13}ON_3S$ requires N = 14.23 per cent.).

Attempts were made by various methods to liberate the free hydrazone from its hydrochloride, but a pure specimen could not be obtained.

In conclusion, we wish to thank the Governors of this College for a scholarship which has enabled one of us (R. B.) to participate in

this investigation. We desire also to thank the Carnegie Trust for the Universities of Scotland for a grant which has partly defrayed the expenses of the work.

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[Received, February 23rd, 1923.]

XCV.—*The Application of the Hofmann Reaction to Substituted Carbamides.*

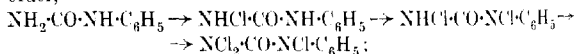
By GEORGE ROBERT ELLIOTT.

SINCE in the reaction between alkali and benzochloroamide the Hofmann reaction proceeds under easily controlled conditions (Elliott, T., 1922, **121**, 202), the possibility of its occurrence with an *N*-chlorocarbamide under similar conditions has been investigated.

The *N*-chloro-compounds of phenylcarbamide were selected for this purpose as likely to give less complex reactions than the analogous derivatives of carbamide itself, owing to the presence of the stabilising phenyl group, and the unsymmetrical structure of the molecule.

According to Doht (*Monatsh.*, 1906, **27**, 213), the action of chlorine in excess on phenylcarbamide in cold acetic acid solution produces 2 : 4-dichlorophenylcarbamide; whilst 2 : 4 : 6-trichloroacetanilide, ammonium chloride, and carbon dioxide are produced at higher temperatures.

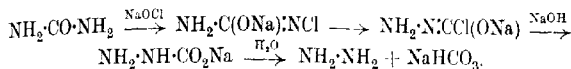
Chattaway and Chaney (T., 1910, **97**, 292), without mention of Doht's experiments, in a much more comprehensive study of the action of chlorine on phenylcarbamide in glacial acetic acid solution, obtained different results from those of the earlier investigator. By variation of the conditions, they substituted chlorine for one, two, or three of the hydrogen atoms attached to nitrogen, in the order,



and in presence of hydrogen chloride, isomerisation of the $-\text{CO}\cdot\text{NCl}\cdot\text{C}_6\text{H}_5$ group to $-\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\text{Cl}$ occurred; the first chlorine atom passes into the para-position, and subsequent atoms then take up the two ortho-positions. Chattaway and Chaney also drew the conclusion that the $-\text{CO}\cdot\text{NHCl}$ group was comparatively stable towards hydrochloric acid, but broke down in presence of alkali carbonates, liberating nitrogen.

The first claim to the successful application of Hofmann's reaction

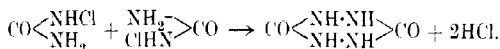
to a carbamide was put forward by Schestakoff (*J. Russ. Phys. Chem. Soc.*, 1905, **37**, 1) when he obtained hydrazine from urea by the action of equivalent quantities of alkali hypochlorite and hydroxide. The suggested mechanism of the reaction was:



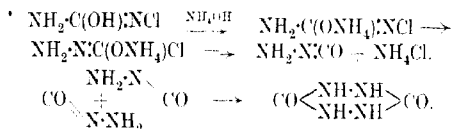
Werner (T., 1922, **121**, 2324), however, from evidence obtained in his investigations on the hypochlorite method of estimating urea, has been led to doubt whether this mechanism can be accepted as applying to more than a possible side reaction.

The experiments described in the present communication tend to support Schestakoff's view that the transformation is analogous to the Hofmann reaction.

Chattaway (T., 1909, **95**, 235) discovered that the action of ammonium hydroxide on dichlorocarbamide, $\text{NHCl}\cdot\text{CO}\cdot\text{NHCl}$, produced *p*-urazine, $\text{CO}\langle\text{NH}\cdot\text{NH}\rangle\text{CO}$; he suggested that monochlorocarbamide was first formed, and under the influence of ammonia was then converted into the urazine by direct condensation, with loss of hydrogen chloride:



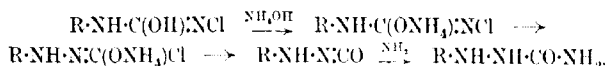
In the author's opinion, however, the change is another instance of the Hofmann reaction, according to the mechanism



As it was unlikely that the intermediate compounds could be isolated, support of this view seemed to require the proof that chlorocarbamides in general react with alkalis through intermediate carbinide compounds.

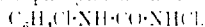
The results actually obtained by the action of sodium hydroxide, ammonium hydroxide, or sodium ethoxide on phenylmonochlorocarbamide, $\text{C}_6\text{H}_5\cdot\text{NH}\cdot\text{CO}\cdot\text{NHCl}$, and on mono- and tri-chlorophenylmonochlorocarbamides are difficult to explain on any other assumption. For instance, the action of ammonium hydroxide on *p*-chlorophenylmonochlorocarbamide produces *p*-chlorophenylsemicarbazide, $\text{C}_6\text{H}_4\text{Cl}\cdot\text{NH}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$. This reaction requires for its simple

explanation the intermediate formation of a carbimide following a Beckmann change, thus :



The action of the other alkalis is similarly explicable on the lines of Hofmann's reaction.

Another surprising and important result came to light in connexion with the preparation of the chlorophenylcarbamides. It was observed that not only can a chlorine atom wander from the nitrogen atom directly attached to the nucleus of a phenylchlorocarbamide, $\text{C}_6\text{H}_5\cdot\text{NCl}\cdot\text{CO}\cdot\text{NHCl}$, for example, giving *p*-chlorophenylchlorocarbamide, $\text{C}_6\text{H}_4\text{Cl}\cdot\text{NH}\cdot\text{CO}\cdot\text{NHCl}$, but also that when the phenyl group is un-substituted, a chlorine atom may wander to the para-position, from the nitrogen atom indirectly attached to the nucleus. Thus, under the influence of alkali in the cold, or by boiling the aqueous solution, *p*-chlorophenylcarbamide, $\text{C}_6\text{H}_4\text{Cl}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$, was obtained from phenylmonochlorocarbamide, $\text{C}_6\text{H}_5\cdot\text{NH}\cdot\text{CO}\cdot\text{NHCl}$. If the para-position be already occupied, no such wandering to the ortho-position will occur; thus a second atom of chlorine could not be introduced into the nucleus by treatment of *p*-chlorophenylmonochlorocarbamide,



This limitation differentiates the wandering from that which takes place from the nitrogen atom directly attached to the nucleus, and indicates that at no period of the transition does the chlorine atom become linked to this nitrogen atom.

EXPERIMENTAL.

Chlorination of Phenylcarbamide.—As it was immaterial to the present purpose whether the benzene nucleus were substituted or not, provided a chlorocarbamide containing the group $\text{NH}\cdot\text{CO}\cdot\text{NHCl}$ were obtained, the direct chlorination of phenylcarbamide in aqueous solution was studied. Analyses of the products showed that, under such conditions, mixtures of mono, di, and trichloro-phenylchlorocarbamides are formed according to varying degrees of acidity and duration of chlorination. By the action of sulphurous acid on the mixed products, at least two consecutive members of the series phenylcarbamide, *p*-chlorophenylcarbamide, 2:4-dichlorophenylcarbamide, and 2:4:6-trichlorophenylcarbamide are usually obtained, but their separation by fractional crystallisation is too tedious to make the preparation of any particular one of them practicable by this method.

Turning to published methods of preparation of the chloro-carbamides, the author drew the conclusion that Chattaway and Chaney (*loc. cit.*) underestimated the effect of hydrochloric acid on the $-\text{CO}\cdot\text{NHCl}$ group. Concentrated hydrochloric acid causes evolution of chlorine from all the phenylchlorocarbamides containing such a group; and although the action is slow with dilute acid, it certainly takes place. Thus if phenylcarbamide be completely chlorinated in concentrated hydrochloric acid solution, using a moderately slow stream of chlorine, 2:4:6-trichlorophenylcarbamide only will be obtained, and no chlorine attached to nitrogen will be detectable in the product. Owing to the hydrogen chloride liberated during substitution, a similar action takes place when the chlorination is conducted in indifferent solvents: this to some extent causes uncertainty in repeating the carefully worked-out preparations of Chattaway and Chaney if a slower stream of chlorine than that used by these experimenters be employed. In repeating their preparation of 2:4:6-trichlorophenylmonochlorocarbamide, $\text{C}_6\text{H}_2\text{Cl}_3\text{NH}\cdot\text{CO}\cdot\text{NHCl}$, which, being the ultimate product of direct chlorination in acetic acid solution, is given as the most easily prepared of the chlorophenylchlorocarbamides, the author carefully fulfilled the prescribed conditions of concentration and temperature. After chlorination for two hours, no product had separated, and on adding water, a mixture containing very little chlorine attached to nitrogen, and consisting mainly of 2:4:6-trichlorophenylcarbamide, was obtained. Too slow a stream of chlorine had, evidently, been employed, so that chlorine was removed from the $-\text{CO}\cdot\text{NHCl}$ group as quickly as it was introduced.

A similar explanation, no doubt, accounts for the failure of Doht (*loc. cit.*) to obtain a chlorocarbamide, although his statement that 2:4-dichlorophenylcarbamide is produced by the action of excess of chlorine on phenylcarbamide in cold acetic acid solution is incorrect.

As direct chlorination of phenylcarbamide offered such difficulties of control, the use of *N*.5 hypochlorous acid was resorted to. By this means, in the cold and in absence of hydrochloric acid, chlorine atoms are introduced in the order given on p. 804.

As, however, the reaction between a carbamide and hypochlorous acid is reversible, an excess of the latter reagent is required for the completion of each of these stages: a 10 per cent. excess of *N*.5 hypochlorous acid was employed in each case, although this amount does not displace the equilibrium in any reaction to the completion point. It was desirable, however, to underchlorinate rather than to overchlorinate, as the presence of unchanged carbamide does not affect the result of the action of alkalis, reversion to carbamide

being one of the normal courses of such reaction with the chloro-carbamide.

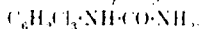
Preparation of Phenylmonochlorocarbamide, $C_6H_5 \cdot NH \cdot CO \cdot NHCl$.—The requisite amount of hypochlorous acid is allowed to remain in contact with a suspension of finely ground phenylcarbamide during several hours. The oily emulsion which first forms soon coagulates to yellow nodules of crude phenylmonochlorocarbamide.

Treated with cold hydrochloric acid, this compound loses chlorine, and phenylcarbamide is obtained; consequently the chlorine atom is combined with the nitrogen atom indirectly attached to the nucleus, otherwise isomerism to *p*-chlorophenylcarbamide would occur. If, however, this chlorocarbamide be warmed with water, chlorine will wander from the side chain to the para-position in the nucleus; in the cold, no *p*-chlorophenylcarbamide could be detected even at the end of twenty-four hours.

Preparation of p-Chlorophenylcarbamide, $C_6H_4Cl \cdot NH \cdot CO \cdot NH_2$.—Phenylcarbamide is treated with an aqueous solution of hypochlorous acid (1 mol.), and the solution heated to boiling. This does not serve to complete the transformation, but a repeated treatment with the acid (1 mol.) is more than sufficient to complete the change without introducing any further chlorine atoms into the nucleus of the *p*-chlorophenylcarbamide already present. Any chlorine attached to nitrogen is now removed with sulphur dioxide, and the brown solution decolorised with animal charcoal. *p*-Chlorophenylcarbamide separates in needles from the cooled solution and after recrystallisation from water melts at 212°.

A second atom of chlorine may be introduced into the nucleus only by causing it to wander from the nitrogen atom directly attached to the nucleus. Attempts were made to prepare 2:4-dichlorophenylcarbamide by treatment of *p*-chlorophenylcarbamide with two equivalents of hypochlorous acid to produce the compound $C_6H_3Cl_2 \cdot NH \cdot CO \cdot NHCl$, warming with a little hydrochloric acid to isomerise to 2:4-dichlorophenylmonochlorocarbamide, and then treating with sulphurous acid. Owing, however, to the complex equilibria between hypochlorous acid, the chlorophenylcarbamide, and the various possible chloro-compounds of mono-, di-, and tri-chlorophenylcarbamides, mixtures of mono- and di-, or of di- and tri-chlorophenylcarbamides were obtained in each case, and could only be separated by tedious fractional crystallisation.

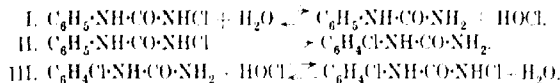
Preparation of 2:4:6-Trichlorophenylcarbamide,



This compound is most easily prepared by direct chlorination to completion of phenylcarbamide (10 grams), dissolved in a mixture of glacial acetic acid (100 c.c.) and concentrated hydrochloric acid

(100 c.c.). The product is precipitated with water, collected, and recrystallised from alcohol. Should the presence of any chlorine attached to nitrogen be indicated on testing with potassium iodide, the product is first treated with sulphurous acid.

Action of Alkalis on Phenylchlorocarbamide, $C_6H_5 \cdot NH \cdot CO \cdot NHCl$.—The preliminary reactions which take place in aqueous solution are represented by:



In each experiment, phenylcarbamide was formed (reaction I); *p*-chlorophenylcarbamide was also produced under the influence of the alkali (reaction II). The further product was actually the result of the action of alkali on *p*-chlorophenylmonochlorocarbamide obtained according to reaction III, and will be considered later. It will be seen that this removal of *p*-chlorophenylmonochlorocarbamide causes each reaction to proceed from left to right by displacement of the equilibria.

The final products of the action of alkalis on phenylchlorocarbamide are consequently identical with those obtained from *p*-chlorophenylmonochlorocarbamide.

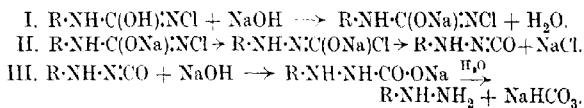
Action of Sodium Hydroxide.—On addition of sodium hydroxide solution to phenylmonochlorocarbamide, $C_6H_5 \cdot NH \cdot CO \cdot NHCl$, there was a development of heat, an odour reminiscent of carbamine, a darkening of the colour, and a vigorous evolution of nitrogen. The chlorocarbamide appeared to be more soluble in the alkali than in water, and the residue after filtration consisted mainly of phenylcarbamide and *p*-chlorophenylcarbamide. As it was the changes of the portion soluble in alkali, probably due to the preliminary formation of a compound $R \cdot NH \cdot CO \cdot ONa \cdot NCl$, which were to be studied, the procedure in each experiment was to add the alkali solution, stir, filter rapidly, and examine the filtrate, rejecting the residue.

The clear filtrate soon became cloudy, and steam distillation yielded (a) a compound (*p*-chlorophenylhydrazine) which reduced Fehling's solution and gave with benzaldehyde a compound which contained chlorine, (b) a yellow oil having the properties of chlorobenzene.

After separating these substances by filtration, the alkaline residue was acidified with hydrochloric acid; it gave a yellow precipitate (*p*-chlorobenzenediazocarboxylic acid and *p*-chlorophenylhydrazinecarboxylic acids), which decomposed instantaneously with a vigorous gas evolution, leaving a pasty, yellow mixture of

products, amongst which chlorobenzene was identified, whilst the acid solution contained *p*-chlorophenylhydrazine, which separated on the addition of alkali.

Although each of these products was only formed in very small quantity, there is little doubt that Hofmann's reaction had taken place according to the following mechanism, where $R = p\text{-C}_6\text{H}_4\text{Cl}$:

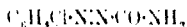


The hydrazine formed would then be attacked by the sodium hypochlorite present in solution, giving the hydrocarbon which is the normal product of such action (Chattaway, T., 1909, **95**, 1065). Complications also arise from the oxidation of the sodium *p*-chlorophenylhydrazinecarboxylate, $\text{C}_6\text{H}_4\text{Cl}\cdot\text{NH}\cdot\text{NH}\cdot\text{CO}_2\text{Na}$, to sodium *p*-chlorobenzenediazocarboxylate, $\text{C}_6\text{H}_4\text{Cl}\cdot\text{N}\cdot\text{N}\cdot\text{CO}_2\text{Na}$. The free diazo-acid decomposes immediately, giving a complex mixture of products, one of which is chlorobenzene.

Action of Ammonium Hydroxide.—Ammonium hydroxide was added to phenylmonochlorocarbamide, and the well-stirred solution was then immediately filtered. The residue consisted mainly of phenylcarbamide and *p*-chlorophenylcarbamide. The clear, orange-coloured filtrate, when allowed to stand, or more rapidly when warmed, deposited a yellow precipitate which reduced warm Fehling's solution. This product proved to be a mixture of two compounds separable by extraction with boiling benzene. The benzene extract deposited long, orange-red needles, which after recrystallisation melted at 182° , whilst the insoluble portion was colourless, and after recrystallisation from acetic acid melted at 233° .

The insoluble, colourless product reduced boiling Fehling's solution, and gave, on hydrolysis, ammonia and colourless needles melting at 90° , which readily reduced Fehling's solution in the cold. The compound (m. p. 233°) was doubtless *p*-chlorophenyl semicarbazide (Found: N = 22.7. $\text{C}_7\text{H}_5\text{ON}_3\text{Cl}$ requires N = 22.64 per cent.). The hydrolysis product (m. p. 90°) was *p*-chlorophenylhydrazine.

On oxidation with alkaline permanganate, the chlorophenyl semicarbazide gave *p*-chlorobenzenediazocarbamide,



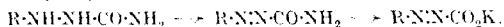
(m. p. 182°), which proved to be identical with the portion of the original product soluble in benzene.

The mechanism of the reactions giving these products is probably

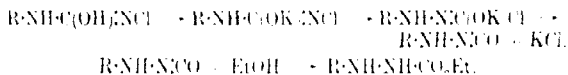
represented by the scheme shown on p. 806, and during the reaction some of the *p*-chlorophenylsemicarbazide is oxidised to *p*-chlorobenzenediazocarbonamide.

It was found that *p*-chlorophenylsemicarbazide is very susceptible to alkaline oxidising agents, and is, indeed, readily oxidised to the diazo-compound if left exposed to the air, in alkaline solution. An alcoholic solution of the semicarbazide rapidly became orange-red after the addition of ammonium hydroxide solution, and deposited long, orange needles of *p*-chlorobenzenediazocarbonamide after exposure to the air for several days.

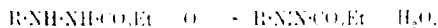
When a solution of the semicarbazide in alcoholic potash is left exposed to the air, golden-yellow flakes appear after about two days. This compound is probably potassium *p*-chlorobenzene-diazocarboxylate, $C_6H_4Cl \cdot N \cdot N \cdot CO_2K$, as its properties and reactions agree in all respects with those of this salt as recorded by Hantzsch and Schultze (*Ber.*, 1895, 28, 2081); its formation is doubtless due to hydrolysis following oxidation:



Action of Potassium Ethoxide. On the addition of potassium ethoxide to an alcoholic solution of phenylmonochlorocarbamide, there was a darkening of the solution and potassium chloride separated, followed after some time by a precipitate of golden-yellow plates. It was found impossible to purify this compound from potassium chloride, but in properties it appeared to be identical with the sample of potassium *p*-chlorobenzenediazocarboxylate prepared from *p*-chlorophenylsemicarbazide as described above. From analogy with previous results, the reaction probably proceeds along the lines



In the presence of alkaline oxidising agents the hydrazo-compound would doubtless oxidise to the diazo-compound,



which by hydrolysis would give $R \cdot N \cdot N \cdot CO_2K$.

The view that the product is a diazo-compound and not a hydrazo-compound is based on its golden-yellow colour, which is not due to organic impurity; also on the fact that the free acid liberated from the potassium salt is obtained as a yellow precipitate before it decomposes.

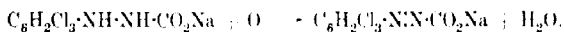
Action of Alkali on 2:4:6-Trichlorophenylmonochlorocarbamide,
 $C_6H_2Cl_3 \cdot NH \cdot CO \cdot NHCl$

Action of Sodium Hydroxide.—If sodium hydroxide be added to the chlorocarbamide, and the product boiled and steam distilled, 2:4:6-trichlorobenzene will be obtained. If, however, the reaction be performed in the cold, other compounds may be isolated.

As before, the alkali was added, the mixture stirred and immediately filtered, and the filtrate and washings were examined.

On the addition of the alkali, heat was developed, and the solution darkened: in some cases, conditions favoured the separation of a brown precipitate of a sodium compound. On acidifying the solution with hydrochloric acid, a yellow precipitate (trichlorobenzenediazocarbonylic acid and trichlorophenylhydrazinecarboxylic acid) separated momentarily, but decomposed immediately with effervescence and production of a brick-red, pasty mass, from which *s*-trichlorobenzene was obtained on steam distillation. After filtration, the acid solution was made alkaline, and a colourless precipitate of 2:4:6-trichlorophenylhydrazine obtained. This compound crystallises from alcohol in long, flat needles melting at 138° (Found: Cl = 50.19. $C_6H_2N_2Cl_3$ requires Cl = 50.36 per cent.). Its warm aqueous solution readily reduces Fehling's solution, and when boiled with copper sulphate gives *s*-trichlorobenzene. The *hydrochloride* is readily soluble in water, but only slightly soluble in concentrated hydrochloric acid.

The mechanism of the reaction may be represented as in the production of *p*-chlorophenylhydrazine; and, as in that case, oxidation to some extent diverts the main reaction, sodium trichlorophenylhydrazinecarboxylate giving sodium trichlorobenzenediazocarbonylate,



The brown precipitate which in some cases separated from the original reaction mixture was probably the oxidation product, sodium 2:4:6-trichlorobenzenediazocarbonylate alone: when treated with acid, it gave a red, pasty mass, similar to that obtained as already described, and no hydrazine could be obtained from the resultant solution.

Action of Ammonium Hydroxide.—The chlorocarbamide was more soluble in ammonium hydroxide solution than in water, but on warming the clear solution, only 2:4:6-trichlorophenylcarbamide separated.

Action of Sodium Ethoxide.—An alcoholic solution of sodium ethoxide was added to trichlorophenylmonochlorocarbamide; the liquid was well stirred, and then filtered. The filtrate was dark coloured and deposited a flocculent precipitate. This compound, washed with alcohol, was quite colourless, did not melt, and was

evidently sodium 2:4:6-trichlorophenylhydrazinecarboxylate, as it dissolved readily in cold water to give a solution which, slowly when kept, more rapidly when warmed, deposited 2:4:6-trichlorophenylhydrazine. Also, the cold aqueous solution, treated with hydrochloric acid, gave a precipitate which immediately decomposed with effervescence, and from the solution, alkali then precipitated trichlorophenylhydrazine.

The original alcoholic filtrate from the sodium trichlorophenylhydrazinecarboxylate contained the oxidation product, sodium trichlorobenzenediazocarboxylate; after diluting with water, and filtering, the clear filtrate gave, when acidified with hydrochloric acid, a yellow precipitate which decomposed with effervescence, yielding a pasty mass containing *s*-trichlorobenzene.

The mechanism of the reactions giving these products is probably similar to that put forward for the action of potassium ethoxide on phenylmonochlorocarbamide.

In conclusion, the author wishes to express his indebtedness to Professor F. S. Kipping, F.R.S., for his continued interest and criticism of this work; also to acknowledge receipt of a grant from the Department of Scientific and Industrial Research which has enabled this investigation to be carried out.

UNIVERSITY COLLEGE, NOTTINGHAM. *Received, February 20th, 1923.*

XCVI.—*Phosphorous Acid Esters. The Influence of the Character of the Groups R', R'', R''' on the Stability of the Molecular Complexes R'R''R'''C·O·PCl₂ and R'R''R'''C·O·P(OH)₂. Part I.*

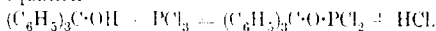
By DAVID RUNCIMAN BOYD and GUY CHIGNELL.

VERY few monoalkyl esters of phosphorous acid have been prepared. Ethylphosphorous acid, $C_2H_5\cdot O\cdot P(OH)_2$, and *iso*amylphosphorous acid, $C_5H_{11}\cdot O\cdot P(OH)_2$, were obtained by Wurtz (*Ann. Chim. Phys.*, 1846, [iii], **16**, 218) from the corresponding alcohols by means of phosphorus trichloride; a similar derivative of methyl alcohol was prepared by Schiff (*Annalen*, 1857, **103**, 164). Carré (*Compt. rend.*, 1901, **133**, 882) has shown that glycolphosphorous acid, $OH\cdot CH_2\cdot CH_2\cdot O\cdot P(OH)_2$, and glycerolphosphorous acid, $C_3H_5(OH)_2\cdot O\cdot P(OH)_2$, are formed by the direct action of phosphorous acid on glycol and glycerol.

These esters, derived from simple aliphatic alcohols, are all

very easily hydrolysed, and with the exception of *isoamylphosphorous acid* they were not obtained in a condition sufficiently pure for analysis. On the other hand, it has been shown by one of us that the phosphorous acid esters derived from the α -di-arylethers of glycerol (T., 1901, **79**, 1221) are comparatively stable compounds. Thus diphenoxyisopropylphosphorous acid, $(C_6H_5 \cdot O \cdot CH_2)_2CH \cdot O \cdot P(OH)_2$, undergoes no change in moist air. It can be crystallised from hot water, and its solution in aqueous ammonia may be boiled for a long period without any decomposition occurring. The influence of the two phenoxy-groups on the stability of the complex $\equiv C \cdot O \cdot P(OH)_2$ is striking, and it appeared probable that stable phosphorous acid esters could be prepared from other alcohols containing one or more phenyl groups. A study of the action of phosphorus trichloride on aromatic alcohols has therefore been undertaken with the object of accumulating data which may lead to a clearer comprehension of the factors by which the stability of the groups $\equiv C \cdot O \cdot PCl_2$ and $\equiv C \cdot O \cdot P(OH)_2$ is determined.

In the majority of the cases so far investigated, it has not been found possible to isolate any phosphorous acid derivative, the products being either chlorides of the type $R'R''R'''Cl$ or unsaturated hydrocarbons. Triphenylcarbinol, on the other hand, when treated with phosphorus trichloride, gives an excellent yield of the corresponding phosphorous acid chloride, in accordance with the equation



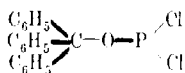
This acid chloride, which can be isolated without difficulty, was found to possess unexpected stability. Unlike any substances of the type $R \cdot O \cdot PCl_2$ hitherto described, all of which resemble phosphorus trichloride more or less closely in properties, *triphenylmethoxyphosphorus dichloride* is not attacked by boiling water or aqueous sodium hydroxide. It can be crystallised from boiling ethyl alcohol with comparatively small loss, provided that the process is carried out rapidly: continued heating with this solvent transforms it into the ethyl ether of triphenylcarbinol. The stability of the compound towards water and alcohol is therefore greater than that of triphenylchloromethane, which, as is well known, is hydrolysed even by cold water, and very rapidly converted into the corresponding ethyl ether by boiling alcohol.

By the action of an alcoholic solution of potassium hydroxide on triphenylmethoxyphosphorus dichloride the corresponding phosphorous acid, $(C_6H_5)_3C \cdot O \cdot P(OH)_2$, can be obtained. This acid shows remarkable stability towards hydrolysing agents. Prolonged boiling of a solution of its sodium salt, in water containing excess

of sodium hydroxide, produces no decomposition. In this respect the acid differs noticeably from diphenoxyisopropylphosphorous acid, which is readily hydrolysed by boiling its solution in aqueous sodium hydroxide.

If the properties of triphenylmethylphosphorous acid are compared with those of its simple prototype, methylphosphorous acid, the salts of which decompose in aqueous solution even at room temperature, it is obvious that the substitution of three phenyl groups for the three hydrogen atoms of the methyl radicle has profoundly affected the capacity of the complex $\equiv\text{C}\cdot\text{O}\cdot\text{P}(\text{OH})_2$ to resist hydrolysis.

An explanation of the remarkable influence of the phenyl groups may be looked for in more than one direction, but at the present stage of this investigation it is not proposed to enter upon a full discussion of the theoretical possibilities. It may, however, be pointed out that the hypothesis of varying affinity values, which has been successfully applied by Werner (*Ber.*, 1906, **39**, 1278) to account for the conspicuous reactivity of the chlorine atom in triphenylchloromethane, does not offer any explanation of the unusual stability of triphenylmethoxyphosphorus dichloride. This is evident from a consideration of the formula



in which the chlorine atoms appear as loosely attached to the phosphorus atom. The behaviour of other triarylecarbinols towards phosphorus trichloride is at present under investigation.

EXPERIMENTAL.

Triphenylmethoxyphosphorus Dichloride.—Ten grams of triphenylecarbinol (1 mol.) were added to 10 grams of phosphorus trichloride (1.9 mols.) contained in a flask which was cooled in ice. After standing for half an hour, the flask was removed from the ice and the reaction was completed by heating in a water-bath under reflux for one hour. The reaction product formed a hard mass with a pale yellow colour. To facilitate its removal from the flask, a small quantity of ether was added and the contents of the flask were poured on ice. The resulting solid product was filtered off, washed with aqueous ammonia and then with water, pressed, and dried in a vacuum desiccator.

In order to remove triphenylchloromethane, which is produced along with triphenylmethoxyphosphorus dichloride by the action of phosphorus trichloride on triphenylecarbinol, the crude product,

after drying, was boiled for two minutes with 20 c.c. of ethyl alcohol. The greater part of the material remained undissolved and, after cooling, was filtered by the aid of the pump, and dried in a desiccator. In this way, 7 grams of nearly pure *triphenylmethoxyphosphorus dichloride* were obtained.

The compound is conveniently recrystallised by dissolving in hot chloroform and adding to the chloroform solution about half its volume of acetone. On cooling, minute colourless plates and prisms separate. These begin to shrink at 180° and melt with decomposition at $189\text{--}190^{\circ}$ (Found: C = 63.23; H = 4.09; P = 8.40; Cl = 19.82. $\text{C}_{19}\text{H}_{15}\text{OCl}_2\text{P}$ requires C = 63.15; H = 4.15; P = 8.59; Cl = 19.63 per cent.).

A determination of the molecular weight in chloroform solution by the Landsberger method gave 352. $\text{C}_{19}\text{H}_{15}\text{OCl}_2\text{P}$ requires $M = 361$.

The substance is moderately soluble in boiling toluene, and difficultly soluble in hot benzene, acetone, or ethyl acetate. It dissolves slightly in boiling ethyl alcohol and crystallises out as the solution cools; but if boiled with alcohol for about half an hour it is converted into triphenylmethyl ethyl ether.

Triphenylmethoxyphosphorus dichloride is not affected by boiling water or aqueous sodium hydroxide. If crystallised rapidly from hot aqueous acetone (10 vols. of acetone to 1 vol. of water), only a comparatively small portion is hydrolysed. It dissolves in cold concentrated sulphuric acid, with evolution of hydrogen chloride, forming an orange-red solution. If this solution is poured into water, a precipitate of triphenylcarbinol is obtained.

Triphenylmethylphosphorous Acid.—Four grams of triphenylmethoxyphosphorus dichloride were mixed with 25 c.c. of an 8 per cent. solution of potassium hydroxide in alcohol (rather more than three mols. of base for one mol. of phosphorous acid chloride), and the mixture was heated in a water-bath under reflux for three-quarters of an hour. The product was mixed with 30 c.c. of water and evaporated to dryness in a steam-bath. The solid residue was treated with about a litre of water, and the liquid was made alkaline by the addition of a small quantity of potassium hydroxide. After boiling and again allowing to cool, the liquid was filtered from undissolved matter. On adding hydrochloric acid to the clear filtrate, a curdy, white precipitate of *triphenylmethylphosphorous acid* formed.

After standing some hours, the precipitate was collected, washed with water containing a little hydrochloric acid, and dried in a vacuum desiccator. The yield was 2.3 grams. The substance is somewhat difficultly soluble in most organic solvents. It was

recrystallised from benzene, from which it separates in clusters of very small plates. These soften at about 230° , and fuse partly, with decomposition, at 237° . Fusion becomes complete at about 247° (Found: C = 70.66; H = 5.49; P = 9.43. $C_{18}H_{17}O_3P$ requires C = 70.33; H = 5.30; P = 9.57 per cent.).

Triphenylmethylphosphorous acid dissolves readily in a hot solution of sodium hydroxide, and the sodium salt of the acid separates as a gelatinous precipitate on cooling the solution. The salt is moderately soluble in cold water: no decomposition occurs on boiling the aqueous solution even in the presence of excess of alkali.

THE UNIVERSITY COLLEGE,
SOUTHAMPTON.

[Received, February 15th, 1923.]

XCVII.—*Tesla-luminescence Spectra. Part II. The Effect of Varying Temperature and Pressure on the Benzene Spectrum.*

By WILLIAM HAMILTON McVICKER and JOSEPH KENNETH MARSH.

IN a previous communication (McVicker, Marsh, and Stewart, this vol., p. 642), a method was described whereby the vapours of a number of compounds of complex structure may be made to emit a spectrum under the influence of a high-frequency electric discharge. Details concerning the benzene spectrum taken at a pressure of 65 mm. at room temperature were given showing that it was composed of more than 50 narrow bands, falling into two series and spaced at equal intervals of frequency between $\lambda\lambda$ 2656 and 3127 Å.U. These bands formed a number of groups each with a strong head band at the short wave-length end, and the main series is calculable from the formula

$$1/\lambda = 98.712/m - 98.712/n, 6$$

where $m = 33, 34, 35, \dots$, whilst n varies from 6 to 0.

Beginning at the end of greater wave-length, these were for convenience designated by the letters A to F. Groups C, D, and E were strong and clear; F was not so strong, and one line of a group G was visible. The whole spectrum was believed to correspond in part with the absorption spectrum of benzene vapour, in part with the fluorescent spectrum, and to be in part new.

Varying conditions of temperature and pressure have been found to produce some changes in the spectrum. Interest centres more particularly in the effect of reducing the pressure to a low figure.

Two further series of bands, G and H, have been observed at a pressure of 1.6 mm., and these, moreover, do not conform to the type previously recorded. In the first place, they are very much feebler. The intensity of the head band of group H was after ninety minutes' exposure no greater than what might have been produced in, say, group D by an exposure of a minute or two. The new series on the whole were not so sharp and the intensity did not fall off so regularly from the head as in previous groups. The head bands of groups F, G, and H have wave-lengths 2667, 2602, 2541 Å.U., respectively, and so are spaced at intervals differing in wave number, $1/\lambda$, by 92 units. Those bands in the G and H series which are sharp are seen to correspond with bands observed in the absorption spectrum of benzene vapour by Henri (*J. Phys. Radium*, 1922, [vi], 3, 181) and to belong to series II and IV in his groups A, B, and C, for which he gives formulæ of the following type :

$$\text{Series II : } 1/\lambda = 3749.4 + 92.14n - (15.9p + 0.2p)$$

$$\text{Series IV : } 1/\lambda = 3742.6 + 92.14n - 16.6p,$$

where n and p are small whole numbers.

Our observations of emission bands are compared with Henri's absorption bands in the following table :

	λ .	$1/\lambda$.	$1/\lambda$.	Henri.	
Band H	2541	3935	3933.7	Band C	Series II
	2553	3917	3917.5		C
	*2590—6	3832—63			II
Band G	2602	3843	3841.5	B	II
	09	33	34.7	B	IV
	2613	3827	3825.4	B	II
	21	16	18.2	B	IV
	2625	3810	3808.9	B	II
	*2631—6	3794—01			
	*2642—7	3779—85			
	2657	3764			
Band F	2662	3756			
	2667	3749	3749.4	B	II

* Broad and indistinct.

The agreement is within our experimental error of about 1 Å.U. The Fraunhofer effect to which attention was directed in our previous paper is here seen to be further exemplified in a striking manner. It is noteworthy that the absorption bands of Henri's series II extend further into the ultra-violet than his other series—right into the region from about $\lambda\lambda$ 2350 to 2150, where benzene is again highly transparent. Beyond this is a second set of absorption bands, and the question arises as to whether under suitable conditions benzene may be able to luminesce or fluoresce in this

transparent region. The probability is that a very low pressure will be found to produce this effect, but we hope to investigate this point shortly.

The spectrum over a range of pressures from 1.6 mm. to 22 cm. corresponding roughly to $M/20,000$ to $M/750$ has been investigated. At pressures of 22 cm. it was less intense and of poorer definition than at 6.5 cm., whilst further there were signs of decomposition and of the carbon spectrum. At 1.6 mm., the bands were sharp, but the reduced quantity of benzene in the observation tube diminished the intensity noticeably. The effect of high pressure is also to curtail the spectrum at the end of short wave-length. At 3.5 cm., band G was very faint and at 22 cm. pressure band F had nearly disappeared also.

The effect of temperature on the spectrum was studied by comparing spectra taken at 15° and at 150° at constant pressure and also at constant volume. It was found that at the higher temperature the bands were decidedly less clear, and the spectrum was also shortened at the end of small wave-length. The effect was thus very similar to that of high pressure. The differences in the spectrum at high temperatures or pressures probably arise from the same cause, namely, the increased number of collisions between the molecules.

EXPERIMENTAL.

The general arrangement of the apparatus was similar to that previously described. For studying the vapour at high temperatures the double iron jacket was filled with mercury and directly heated. For pressures down to 3 cm. a flask containing benzene was attached to the inlet tube and a flask cooled in a freezing mixture to the outlet. A water-pump sufficed to evacuate the apparatus. For the higher pressures the flask of benzene required slight heating, and an air leak into the water-pump was arranged. For pressures below 3 cm., a Volmer mercury vapour jet pump was used in conjunction with the water-pump, and a fine adjustment glass stop-cock was inserted between the reservoir of benzene and the observation tube. The pressure could be regulated by allowing a more or less rapid stream of vapour past the stop-cock. The pressures were read on a mercury gauge with the aid of a travelling microscope. A limit of about 1.6 mm. was set in the present work by the fact that although a pressure of 0.1 mm. or less could readily be attained, yet at low pressures slight traces of air gave rise to a powerful glow completely masking the benzene spectrum.

From the foregoing it is seen that the Tesla-luminescence spectrum of benzene is characteristic and persists over a large range of experi-

mental conditions. Complete disruption of the benzene molecule which would be quickly brought about by an ordinary high potential discharge is with the high-frequency discharge entirely avoided at low pressures. In fact, the high-frequency discharge appears to have rather the reverse effect at low pressures, for small quantities of an orange-coloured product rather like shellac in appearance are found to collect in the observation tube. This is presumably a condensation product of benzene.

The form of the spectrum is very similar to that of some other vapours such as sodium or iodine which have been studied by R. W. Wood and which show channelled or fine banded structure, either by the absorption or fluorescent method, when studied at low pressures and at not too high temperatures. The spectrum is also similar to that of fluorescing benzene vapour (see following paper). This correspondence is also found to hold in the case of other compounds under investigation at present, so that a promising line of attack on the problems of absorption and fluorescent spectra is presented.

THE SIR DONALD CURRIE LABORATORIES,
QUEEN'S UNIVERSITY, BELFAST.

[Received, March 12th, 1923.]

XCVIII.—*The Fluorescence Spectrum of Benzene Vapour.*

BY WILLIAM HAMILTON McVICKER and JOSEPH KENNETH MARSH.

OBSERVATIONS on the fluorescence spectrum of solutions of benzene have been made by Stark, Dickson, Henri, and others with differing results, as the following table shows, in which the wave-lengths of the heads of the several bands are given.

Stark (1907)		272	280	283	292
Dickson (1912)	2599	2635	2679	2754	2827 2910
Henri (1922)		2659	2702	2766	2847 2917 3005

In a recent paper (McVicker, Marsh, and Stewart, this vol., p. 642), we gave some particulars of the spectrum of benzene as excited by a high-frequency discharge (see also preceding paper). The heads of the series of bands which were then recorded seemed in good agreement with the positions of the fluorescence bands in alcoholic solution recorded by Dickson if due allowance was made for the effect of the solvent in shifting the bands in the direction of greater wave-length. Dickson also records that he was unable to detect

any fluorescence from the vapour of benzene, and no other experimenters have recorded any. Nevertheless, in order if possible to make a direct comparison of our Tesla-luminescence bands with the fluorescent spectrum some experiments were undertaken which have been at once successful in showing that benzene vapour is capable of fluorescing at a pressure of a few centimetres of mercury.

EXPERIMENTAL.

A piece of silica tubing about 10 cm. long and 2 cm. in diameter was ground off flat at one end and closed by a quartz plate. At the other end, inlet and outlet tubes were inserted through a rubber stopper. The inlet tube was attached to a flask containing pure benzene and the outlet tube to a flask cooled in ice, and the whole apparatus was evacuated by a water-pump.

The quartz end of the silica tube was placed about 2 cm. in front of the slit of the spectrograph. About 4 cm. from the quartz plate and to one side of it was set up a spark gap with iron electrodes. Round the spark gap was placed an opaque screen in which was cut a slit so as to allow a beam of light to fall on the silica tube and its contents immediately behind the quartz plate. On starting the water-pump, distillation occurred from the flask containing benzene through the silica tube to the cooled flask. After a time the benzene froze owing to evaporation and the pressure fell to 3 cm. of mercury. An exposure of 100 minutes sufficed to produce a thin negative showing, however, more than 30 bands. Side by side on the same plate the Tesla-luminescence spectrum of benzene at the same pressure was recorded. In another experiment the iron spark was replaced by the iron arc, so that there was no possibility of electrical excitation, but the spectrum was still obtained.

On comparing the two spectra as produced above, it was apparent that they were the same in structure though differing much in intensity. The fluorescent spectrum showed bands belonging to all the groups B to G, but was very much fainter than the spectrum excited electrically with an exposure only one-fourth as long. It is thus seen that to obtain the same photographic result exposures many times longer are required by the fluorescent method than are necessary with our electrical excitation unless, indeed, an exceedingly intense light source is used.

In the following table the fluorescence bands observed are recorded in wave-lengths. They fall into the groups shown with strong bands at the end of smaller wave-length, and may be divided into two series, for the weaker of which only the last two figures of the

number expressing the wave-length in Ångström units are set down.

Group G.	F.	E.	D.	C.	B.
	2667	2739	2815	2895	2980
	74	47	25	03	2995
	2678	2751	2828	2909	
	85	57	36	17	
	2691	2765	2841	2923	
	97	70	48	2937	
	2702	2777	2855	2950	
	2714	2789	2867	2963	
2657	2729	2802	2880		

It is noteworthy that Group F of fluorescence bands corresponds in position with a series of absorption bands observed by Hartley in benzene vapour (Hartley, *Phil. Trans.*, 1908, **208**, 519). From these results we feel satisfied that under all conditions there is every reason to expect complete similarity between the Tesla-luminescence and the fluorescence of benzene.

THE SIR DONALD CURRIE LABORATORIES,
QUEEN'S UNIVERSITY, BELFAST. *(Received, March 12th, 1923.)*

XCIX.—*Studies of Electrovalency. Part I. The Polarity of Double Bonds.*

By THOMAS MARTIN LOWRY.

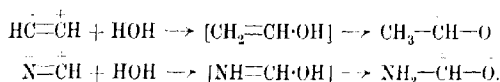
1. *Mixed Double Bonds.*

THE object of this paper is to suggest that, whilst a single bond may be either a covalency or an electrovalency, a *double bond in organic chemistry usually reacts as if it contained one covalency and one electrovalency*. Acetaldehyde is therefore written as $\text{CH}_3\text{CH}=\text{O}$ and ethylene as $\text{CH}_2=\text{CH}_2$. Bonds of this character are described as "mixed double bonds." Their existence can be justified on the basis of the electronic theory of valency by assigning a complete octet to each negatively charged atom, and a sextet of electrons to each positively charged atom (compare G. N. Lewis, *J. Amer. Chem. Soc.*, 1916, **38**, 775; Latimer and Rodebush, *ibid.*, 1920, **42**, 1429; Eastman, *ibid.*, 1922, **44**, 438). Each $\cdot\cdot$ sign then indicates an excess of one planetary electron above the net nuclear charge, and each \cdot sign a deficit of one electron.

2. *Triple Bonds.*

The double bond in oxygen and the triple bond in nitrogen gas may be pure covalencies, since both gases are very inert, unless

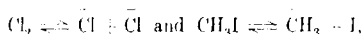
activated, for example, by heat or by an electric discharge. Acetylene and hydrogen cyanide, however, are active polar compounds, to which a mixed triple bond may be assigned. Their hydrolysis by water is then represented by the equations



3. Unsaturation and Reactivity.

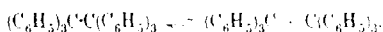
Elements linked by electrovalencies react more readily than those linked by covalencies. The wide difference between the reactivity of single and double bonds therefore finds a simple explanation in the ready development of electrovalencies in the latter. The contrast between acetylene and nitrogen also finds a partial explanation on similar lines.

The reactivity of chlorine and of methyl iodide probably depends on the readiness with which a covalency gives place to an electrovalency, as in the balanced equations,

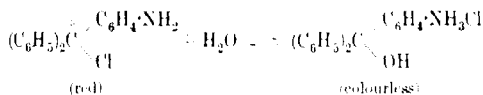


where a double-octet is represented as breaking down into an octet and a sextet in the dissociation which must precede or accompany chemical change in these compounds.

A similar dissociation may be used to account for the electrolytic conductivity of triphenylmethyl,



and for the peculiar properties of von Baeyer's "carbonium" bond (*Ber.*, 1905, **38**, 1156),



I am indebted to Dr. Lapworth for the further suggestion that zinc methyl and the Grignard agent probably owe their special

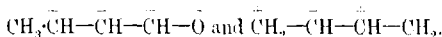
reactivity to the fact that they contain a methyl-ion, as in $\text{Zn} \begin{array}{l} \nearrow \text{CH}_3 \\ \searrow \text{CH}_3 \end{array}$
and $\text{Mg} \begin{array}{l} \nearrow \text{CH}_3 \\ \searrow \text{CH}_3 \end{array}$.

4. *Partial Valencies.*

The theory of partial valencies was introduced by Thiele as a means of expressing the subdivision of affinity between atoms. There is strong evidence, especially from the X-ray analysis of crystals, to show that covalencies are limited to certain directions round an atom, and cannot be split up into smaller units, whilst electrovalencies can be subdivided, for example, into six equal parts in a crystal of rock-salt. The superposition of an electrovalency on a covalency therefore provides a convenient explanation of the subdivision of affinity, which Thiele indicated by dotted lines in unsaturated groups such as $\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{C}}}-\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{C}}}$, $\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{C}}}=\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{O}}}$, or $\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{C}}}=\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{N}}}$. These may be written as $\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{C}}}-\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{C}}}$, $\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{C}}}-\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{O}}}$, and $\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{C}}}-\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{N}}}$, where oxygen and nitrogen are usually negative relatively to carbon, and oxygen relatively to nitrogen.

5. *Conjugated Compounds.*

Crotonaldehyde and butadiene are formulated as



It will be seen that under this scheme the *distinction between single and double bonds in a conjugated system disappears completely*. There is therefore no longer any need to postulate a "wandering of the double bond" when butadiene is brominated, since the central double bond is already in position.

6. *Polarity of Conjugated Compounds.*

(a) The theory of mixed double bonds makes all conjugated systems polar; but the alternate polarities do not extend beyond the last double bond. The alternate polarities discussed by Lapworth and by Kermack and Robinson (T., 1922, **121**, 416 and 427) are therefore confined within the limits of the conjugated system instead of being continued beyond it. Moreover, the promiscuous scattering of $+$ and $-$ signs on alternate atoms is strictly prohibited under the system now put forward, since a covalency must be obliterated whenever an electrovalency is introduced; and on every occasion when the sign $+$ or $-$ is written, a bond $—$ must be deleted in the conventional formulae.

(b) The electronic formulae of Lapworth and of Kermack and Robinson give, when analysed, an excess or deficit of half an electron on the terminal atoms of a conjugated chain, but make the intermediate atoms neutral. The new formulae, on the other hand, indicate that, whilst the main polarity and unsaturation are at the ends of the chain, the alternate polarities and unsaturation

exist also in the intermediate atoms. They therefore provide a simple explanation of the fact that butadiene can be brominated in the 1:2- as well as in the 1:4-position; phenylbutadiene in the 3:4- and diphenylbutadiene in the 1:2-position; and hexatriene in the 3:4-position.

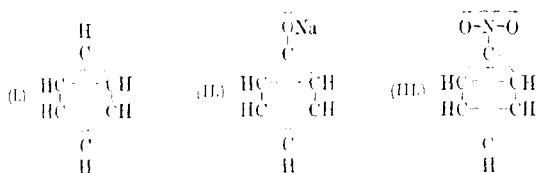
7. Crossed Polarities.

The type of conjugation postulated above differs from that of Thiele (*Lanalen*, 1899, **308**, 337) in that it may be destroyed by crossed

polarities, as in maleic acid, $\bar{\text{O}}-\bar{\text{C}}(\text{OH})-\overset{+}{\text{CH}}=\overset{+}{\text{CH}}-\overset{+}{\text{C}}(\text{OH})-\bar{\text{O}}$, which cannot now be formulated as a conjugated compound. These crossed polarities provide a novel explanation of the instability of compounds of the maleic acid type, as illustrated by (i) the conversion of citraconic into itaconic acid by boiling with soda, $\text{HO}\cdot\text{CO}\cdot\text{CMe}=\text{CH}\cdot\text{CO}\cdot\text{OH} \rightarrow \text{HO}\cdot\text{CO}\cdot\text{C}(\equiv\text{CH}_2)\cdot\text{CH}_2\cdot\text{CO}\cdot\text{OH}$, (ii) the conversion of Δ^2 into Δ^1 -tetrahydrophthalic acid (von Baeyer, *Annalen*, 1890, **258**, 145), (iii) the loss of carbon dioxide as well as water in the oxidation of dihydrophthalic acid (von Baeyer, *ibid.*, 1892, **269**, 178), (iv) the inability of Thorpe and his colleagues to prepare ethyldienemaleic acid, $\text{CH}_3\cdot\text{CH}=\overset{+}{\text{C}}\overset{+}{\text{C}}\cdot\text{CO}\cdot\text{OH}$.

8. Aromatic Compounds.

(a) Benzene (I), sodium phenoxide (II), and nitrobenzene (III)



are formulated as conjugated systems, in which alternate polarities are carried round the carbon atoms of the ring and out into the side-chains. The six hydrogen atoms are, however, neutral, as well as the substituents, since the $+$ and $-$ charges on the latter must balance unless they are ionised.

(b) In the conjugated formulae set out above, every $+$ or $-$ combination may become a reactive centre. The normal points of attack are the electrovalencies of the side-chain, from which substituents may swing down into the ring. But the electrovalencies of the ring may also be attacked directly, giving rise to intermediate *additive* products, either in a 1:2- or in a 1:4-position,

since (as Thiele has pointed out) the latter is the normal behaviour of a conjugated compound.

(c) Bragg's boat-shaped formula for benzene (T., 1922, **121**, 2783) is the *cis*-form of I. In this formula, the oppositely-charged atoms 1 and 4 are on the same side of the plane of the four atoms 2, 3, 5, 6, instead of on opposite sides. This representation provides a particularly simple explanation of the *para*-reactions of benzene, since the *cis*-formula lends itself to this type of action even more readily than the *trans*-formula.

(d) The opposite polarities of II and III correspond with their different behaviour on substitution. The laws of substitution can be stated best in the form that *derivatives with crossed polarities are less stable than those in which the polarities are concordant throughout the conjugated system*. Similarly-polarised groups therefore tend to occupy a *meta*-position relatively to one another, as in *m*-dinitrobenzene and benzene-*m*-disulphonic acid, or in the potassium derivative of resorcinol, $C_6H_4(OK)_2$, which can be produced by fusing with potash a number of simple derivatives of benzene. The halogens, however, behave like amphoteric electrolytes. $Cl_2 \rightleftharpoons \bar{Cl} + \bar{Cl}$, and give disubstitution products occupying an *ortho*- or *para*-position to one another.

(e) These conditions do not prevent side reactions from taking place, which may give rise to compounds with crossed polarities; nor do they prevent these from being produced by indirect processes. The influence of crossed polarities can, however, be detected in the ready displacement by an amino-group of a nitro-group which is *ortho* to a second nitro-group (Meldola, T., 1906, **89**, 1938), since this replacement renders the crossed polarities concordant.

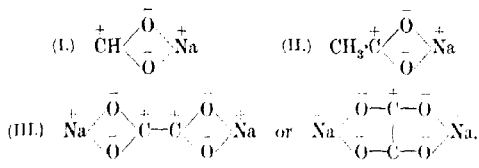
(f) Similar formulæ can be assigned to naphthalene and anthracene, but these differ from the formula for benzene in that the atoms which are common to two rings are surrounded by *three* atoms of opposite sign, representing a further subdivision of the electrovalency into partial valencies.

(g) When the ultimate limit has been reached and the aromatic compound has become a sheet of pure graphite, the new theory provides it with a surface of positively-charged atoms and one of negatively-charged atoms. This gives an almost unique structure in which the bonds within a sheet or double layer of atoms are all covalencies, whilst successive sheets are held together by electrovalencies.

9. Carboxylic Acids.

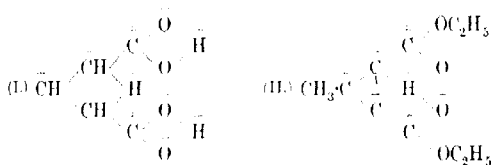
(a) Whilst the theory of mixed double bonds introduces an element of dissymmetry into conjugated compounds, it introduces

a new element of symmetry in the formulæ of the ions of carboxylic acids, of tautomeric ions, and of co-ordinated compounds, since in all these cases *the distinction between the single and double bonds disappears*, just as in other cases of conjugation. Thus sodium formate, acetate, and oxalate become I, II, and III :



In compounds of this type the sodium cannot neutralise either of the negative charges by forming a covalency, since this implies the addition of electrons to an element that already has as many as it can carry. The metal is therefore pictured as occupying a co-ordinated position, in which it is disposed symmetrically (compare Hantzsch, *Ber.*, 1917, 50, 1438) in reference to two negatively-charged oxygen atoms.

(b) A similar co-ordinated position may be assigned to the mobile hydrogen in glutaric acid (I) (Thorpe, *T.*, 1905, 87, 1680) and in ethylenemaleic ester (II) (Goss, Ingold, and Thorpe, *this vol.*, p. 327). In these cases, however, the kation is placed between two —CH— groups instead of between two negatively-charged oxygen atoms.



A study of the models suggests that in the latter compound at least the hydrogen-ion may be symmetrically placed in reference to *four* negatively-charged groups; and this further co-ordination may well be a decisive factor in making possible the isolation of the ionised form of the ester.

(c) The symmetrical formula assigned on similar grounds to the CO_3 -ion is in harmony with crystallographic data. The lesser symmetry of the ClO_3 -ion finds a natural explanation in the presence of a complete octet instead of a sextet of L-electrons round the kernel of the central atom.

10. *Tautomeric Ions. Electrotropy and Prototropy.*

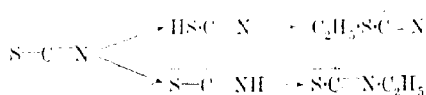
(a) In the light of our present knowledge of the structure of matter it is possible to distinguish clearly two special cases of the general phenomenon of dynamic isomerism, namely:

(i) *Electrotropy*, or reversible change in electromers, which differ only in the arrangement of the electrons (H. S. Fry, "Electronic Conception of Valence," p. 11).

(ii) *Prototropy*, or the reversible change of protomers, which differ from one another in the position of a proton or hydrogen nucleus.

The general case, in which the isomerides may differ in the relative position of radicles other than hydrogen, is classified most conveniently according as the isomeric change is obviously reversible or *allelotropic* (Knorr, *Annalen*, 1899, **306**, 332), or is so nearly complete that reversal can only be detected by indirect methods, for example, by the preparation of derivatives of a labile form, as in the case of ϵ -isatin, or by means of actions such as the bromination of acetone or the racemisation of carboxylic acids, in which the existence of a labile enolic form can be postulated as an intermediate product. This case has been described as *pseudomerism* (von Baeyer, *Ber.*, 1883, **16**, 2188) or as *merotropy* (Michael, *Annalen*, 1908, **363**, 20), the latter term being defined by the characteristic "that a body of stable constitution goes over into the derivative of an isomer."

(b) The theory of mixed double bonds throws a new light on these phenomena, since it assigns identical formulae to the tautomeric ions of isodynamic compounds. An examination of a series of typical formulae shows that a *tautomeric ion is one that can be written in two different ways because there are two points at which a hydrogen nucleus or a radicle can be attached*. The two forms of the ion are tautomeric, in the sense of Laar's original definition, since they are "not isomeric but identical"; but they yield protomeric hydrides, and isomeric derivatives with radicles such as methyl and ethyl. Thus, the tautomeric ion, $\text{--S--C}\equiv\text{N}$ or $\text{S--C}\equiv\text{N--}$, of thiocyanic acid can now be represented by a single formula, from which two protomeric acids and two isomeric ethyl derivatives may be derived, as in the scheme

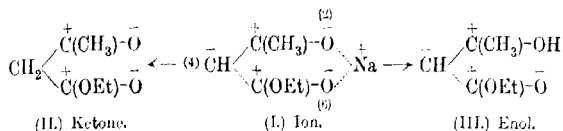


In this case, the two forms of the acid have not been isolated, but the isomeric esters are well known

(c) In the same way, the two forms of ethyl acetoacetate,

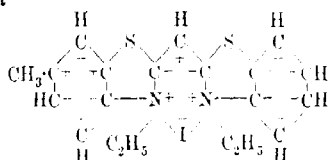


may be derived from a common ion, as in the following scheme :



The tautomeric ion (I) has three negatively-charged atoms to which a hydrogen nucleus may be attracted, but it is usually assumed to settle down in the position (2) or (4). It therefore gives two protomeric hydrides, namely, an enol (III), in which the conjugated system is maintained almost intact (Thiele, *Annalen*, 1899, 308, 337), and a ketone (II), in which it is broken up into two separate double bonds.

(d) Whilst tautomeric ions are usually bipolar anions, precisely similar phenomena may occur in bipolar cations, as in the thiocyanines (Mills and Brauholtz, T., 1922, 121, 1490), where a mobile iodine atom is attracted by two positively charged nitrogens, as in the formula



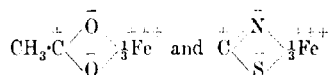
Both nitrogen atoms are quaternary ions, which (like a metal) are unable to accept additional electrons. The iodine is therefore unable to form a covalent bond with either atom, and appears to settle down in a symmetrical position between them (compare sodium acetate). It will be seen that, in this method of representation, the central ring-system corresponds very closely with that of benzene or pyridine, from which it differs mainly in that two of the covalencies are suppressed and the iodine is held in place by electrovalencies only. In this respect it may be compared with Morgan's formula for the acetylacetonates (T., 1914, 105, 193).

11. Co-ordination.

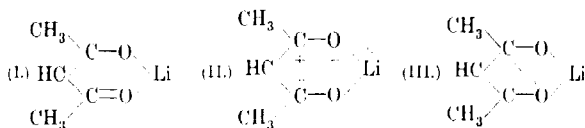
(a) The theory of mixed double bonds has revealed an unexpected relationship between tautomerism and co-ordination, since it appears

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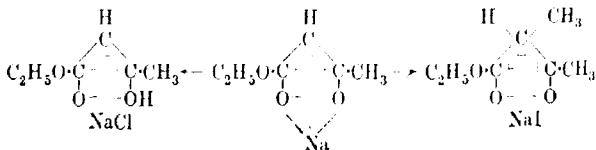
that tautomeric ions in general should tend to form co-ordinated complexes. Thus iron, in its co-ordinated compounds, usually acquires possession of six instead of three radicles, as in the ferri-oxalates. In the case of a tautomeric ion, the metal adheres to *both* of the alternative points of attachment, and so gives rise with special ease to co-ordination. The use of ferric chloride as a reagent for detecting enols therefore appears as a test for bipolar or tautomeric ions by the production of a co-ordinated complex; for example, the red colour of ferric acetate and of ferric thiocyanate can be attributed to co-ordinated complexes of the type



(b) The conventional formula (I) for the acetylacetone complex makes a distinction between (i) a double and a single bond between carbon atoms, (ii) an alcoholic and ketonic oxygen, (iii) a principal and a supplementary valency. When polar double bonds are used, the tautomeric ion becomes completely symmetrical as in II, and the co-ordination complex may be compared with the closely analogous oxalates



Formula II may be compared with the symmetrical formula III put forward by Morgan (T., 1914, **105**, 193), who compares formula I with Kekulé's formula for benzene, and suggests that the two alternative forms may oscillate through the centric phase III. This analogy with benzene is confirmed in the new formulæ now under discussion. Thus the action of hydrogen chloride and of methyl iodide on ethyl sodioacetoacetate can be formulated as involving the formation of 1:2- and 1:4-addition compounds followed by the removal of sodium chloride or sodium iodide:



Summary.

(a) The introduction of electrovalencies into organic chemistry provides a uniform interpretation of (i) unsaturation, (ii) reactivity, especially in compounds such as zinc methyl and the Grignard agent, (iii) partial valencies, (iv) conjugation, (v) alternate polarities, (vi) crossed polarities in conjugated compounds, (vii) the structure of benzene, (viii) the laws of substitution in benzene, (ix) crossed polarities in benzene, (x) the structure of naphthalene, anthracene, etc., (xi) the crystal structure of graphite, (xii) the structure of carboxylic acids, (xiii) the structure of the glutacnic acids, (xiv) tautomeric or bipolar ions, (xv) co-ordination, (xvi) the relation between tautomerism and co-ordination.

(b) Various symbols have been used from time to time by organic chemists in the attempt to represent electrovalencies, for example, the zigzag single and double bonds of von Baeyer, the dotted lines and parentheses of Thiele, the brackets of Hantzsch, the principal and supplementary valencies of Werner, the centric bonds of Armstrong and von Baeyer, and the *para*-bond of Dewar's formula for benzene. All these can now be replaced by the \pm sign which is used universally to represent electrovalency in compounds such as sodium chloride.

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[Received, March 14th, 1923.]

*V.—The Action of Methyl Sulphate on Diphenylamine
and on Methylidiphenylamine.*

By CHARLES STANLEY GIBSON and DUDLEY CLOETE VINING.

IN connexion with another investigation we required some quantity of methylidiphenylamine and ethyldiphenylamine and consequently we have been led to study somewhat closely the action of methyl sulphate and, to a less extent, ethyl sulphate, on diphenylamine. Ullmann, who after Claesson and Lundvall (*Ber.*, 1880, **13**, 1700) developed the use of methyl sulphate as a methylating agent, studied its action on diphenylamine and described the preparation of methylidiphenylamine (*Annalen*, 1903, **327**, 104). On carefully repeating Ullmann's work, we have not been able to obtain the high yield (79 per cent.) of the tertiary base, and we have found that a quaternary compound and a monosulphonic acid of methylidiphenylamine appear to be normal products of the reaction carried out under the conditions described by him. The sodium salt of methylidiphenylaminesulphonic acid we have proved to be

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on diphenylamine in the presence of a suitable alkali, that is, under conditions which minimise the possibility of any sulphonation of methyldiphenylamine taking place. We have also shown that the production of sodium methyldiphenylaminesulphonate by the action of methyl sulphate on diphenylamine or on methyldiphenylamine is to be preferred above the sulphonation of methyldiphenylamine by means of concentrated sulphuric acid.

The aniline salt is the only derivative of methyldiphenylamine-sulphonic acid so far described which has a definite melting point ($179-180^\circ$) and, after melting, the product solidifies at a definite temperature ($195-196^\circ$).^{*} The solid product resulting in quantitative yield is sulphanilic acid, and methyldiphenylamine is formed at the same time. An investigation of the decomposition by heat of the aniline salts of other sulphonic acids is in progress in order to determine whether this mode of decomposition is unique.

Incidentally, we have examined the properties of methyldiphenylamine and we describe a convenient method for the preparation of diphenyldimethylammonium iodide.

We have obtained no definite indication of the formation of a sulphonic acid of ethyldiphenylamine. We have prepared ethyldiphenylamine by the action of ethyl sulphate on diphenylamine, according to Ullmann's method, and observed the formation of ether during the reaction.

We are continuing the investigation of methyldiphenylamine-sulphonic acid with a view to its definite orientation and the examination of its more important derivatives.

EXPERIMENTAL.

The Reaction between Methyl Sulphate and Diphenylamine, and the Preparation and Properties of Methyldiphenylamine.

For the investigation of the reaction at the ordinary temperature, 16.9 grams (1 mol.) of diphenylamine, 12.6 grams (1 mol.) of methyl sulphate,[‡] and 150 c.c. of pure toluene were mixed together, when no rise in temperature was noticed. After standing for forty-eight hours, there was no sign of crystallisation. The solution was then divided into two equal portions. Cooling in ice, one half was carefully treated with a slight excess of sodium hydroxide solution, and the washed toluene layer shaken with an excess of concentrated

^{*} In this connexion, it is worthy of record that A. G. Perkin and S. well (*J. Soc. Chem. Ind.*, 1923, **42**, 277) have recently recorded the convenience of the use of arylamine (especially aniline) salts for the identification and purification of anthraquinone-sulphonic acids.

[‡] The methyl sulphate used throughout the work was very carefully purified. It was neutral in reaction and had a boiling point of $75-77^\circ/12$ mm.

hydrochloric acid. The white, crystalline material which separated weighed, after drying, 10.2 grams; it melted at $179\text{--}181^\circ$ with decomposition and was identical in all respects with a specially prepared specimen of diphenylamine hydrochloride. The amount of diphenylamine hydrochloride recovered showed that 99.4 per cent. of the original diphenylamine was unchanged. The other half of the toluene solution, after standing for five weeks, had deposited a quantity of colourless plates which were somewhat hygroscopic and melted with slight decomposition at $123\text{--}127^\circ$. The substance was sparingly soluble in water, and its cold hydrochloric acid solution gave no precipitate with a solution of barium chloride, but on boiling barium sulphate was gradually precipitated. On treatment with an excess of aqueous caustic soda, the crystals yielded an oil which, from its benzene solution, was converted into diphenylamine hydrochloride (m. p. 179° with decomposition). The amount of diphenylamine hydrochloride obtained represented 23.7 per cent. of the base originally taken, and the crystals which separated from the toluene solution were evidently the hydrogen methosulphate of diphenylamine. The mother-liquor from the crystals of the hydrogen methosulphate was carefully mixed with an excess of aqueous caustic soda and the toluene solution mixed with concentrated hydrochloric acid. Diphenylamine hydrochloride separated and the filtrate from this, when treated in the usual manner, gave methyldiphenylamine (b. p. $290\text{--}292^\circ$). The amount of methyldiphenylamine obtained corresponded to 23 per cent. of the original diphenylamine taken, whilst 72 per cent. was recovered as diphenylamine hydrochloride.

After the preliminary experiments, in which the conditions described by Ullmann (*loc. cit.*) were adhered to as far as possible, had indicated (1) that the yield of methyldiphenylamine obtained was much less than that obtained by Ullmann, (2) that the alkaline liquid contained a considerable quantity of a sodium salt of a monosulphonic acid of methyldiphenylamine, and (3) that from the alkaline liquid a heavy oil separated from which derivatives of diphenyldimethylammonium hydroxide were readily obtained, it was found that the reaction could be carried out either in the presence or absence of benzene, and that the reacting quantities of diphenylamine and methyl sulphate, and the time of heating, could be varied considerably without greatly affecting the results. In all cases, the reaction was accompanied by the formation of a volatile substance, probably a mixture of methyl alcohol and dimethyl ether, which usually escaped condensation. The following is a description of one of many experiments.

33.8 Grams (1 mol.) of diphenylamine, 37.8 grams (1.5 mols.)

of methyl sulphate, and 75 c.c. of pure benzene were heated on a water-bath under a reflux condenser for three hours, and the benzene was then separated by steam distillation. After cooling, a slight excess of sodium hydroxide solution was added, when the crude base separated as an oil on the surface and a quantity of a somewhat viscous oil separated at the bottom of the alkaline solution. The whole mixture was further diluted with water and boiled vigorously for about thirty minutes, when the heavy oil (p. 834) no longer separated as a definite layer. The cold alkaline solution deposited colourless crystals, the sodium salt of methyldiphenylaminesulphonic acid (p. 836), and to facilitate the separation of the base the alkaline solution was kept at about 50° during the extraction with benzene. The washed benzene solution was shaken and then allowed to stand for some hours with concentrated hydrochloric acid, and the diphenylamine hydrochloride which separated was filtered off and dried (weight = 6.1 grams). Methyldiphenylamine was isolated from the hydrochloric acid solution of its hydrochloride in the usual manner and finally distilled under ordinary pressure: the fraction boiling at 291–292° and collected between 290° and 295° weighed 18.1 grams. It was found to be almost pure methyldiphenylamine and corresponded to a yield of 49.5 per cent. of the theoretical. This is the highest yield of the base we have obtained under the conditions described by Ullmann, whereas he stated that he obtained a yield of 79 per cent. of the theoretical and did not describe either the formation of a methyldiphenylaminesulphonic acid or of a heavy oil, which is chiefly diphenyldimethylammonium hydroxide. The amount of sodium methyldiphenylaminesulphonate obtained in the experiment described was 6.4 grams.

As far as the preparation of methyldiphenylamine itself is concerned, it seemed clear that the conditions should be such as to minimise any sulphonation or formation of a quaternary compound. The following is a description of a typical preparation of the tertiary base.

A mixture of 33.8 grams (1 mol.) of diphenylamine and 37.8 grams (1.5 mols.) was heated for about ten minutes in a water-bath, when the formation of dimethyl ether was noticed. A solution of 35 grams of anhydrous sodium carbonate in 200 c.c. of water at a temperature of 50° was then run into the mechanically stirred mixture during three hours. The mixture was extracted with benzene and the washed benzene solution shaken and then allowed to stand with 50 c.c. of concentrated hydrochloric acid. The diphenylamine hydrochloride was filtered off and dried. It weighed 5.9 grams. The filtrate from this was made alkaline, when the liberated base dissolved in the benzene layer. The benzene solu-

tion after washing and drying was distilled. The tertiary base distilled almost entirely at 291—292°, and the distillate, almost pure methyldiphenylamine, weighed 25.5 grams. Allowing for the unchanged diphenylamine recovered as hydrochloride, the actual yield of methyldiphenylamine obtained was 79.4 per cent. of the theoretical quantity.

Some uncertainty exists as to the boiling point of methyldiphenylamine. We have found the boiling point of the pure base to be 291—292° under atmospheric pressure and 145—145.5°/10 mm. The pure base is a pale yellow oil which gradually acquires a faintly red colour on exposure to air. It was identified by conversion into its chloroplatinate, which separated in lustrous, golden-yellow, prismatic needles on mixing alcoholic solutions, containing hydrochloric acid, of the base and platinum chloride (Found: Pt = 25.14. Calc., Pt = 25.15 per cent.). The compound melted and decomposed at 207—209°.

Salts of Methyldiphenylaminesulphonic Acid.

Sodium Salt.—It has been remarked that in working up the reaction product of methyl sulphate and diphenylamine according to Ullmann's method an appreciable quantity of a sodium salt of methyldiphenylaminesulphonic acid was always obtained. It was found to be almost pure, and later was shown to be identical with the sodium salt of methyldiphenylaminemonosulphonic acid prepared by Cloëz (*loc. cit.*), who, however, did not obtain it pure.

The salt is readily soluble in water and sparingly soluble in a dilute solution of sodium hydroxide. It is insoluble in pure ethyl alcohol and crystallises from water in beautiful, colourless, glistening plates containing two molecules of water of crystallisation (Found: $H_2O = 11.7$. $C_{13}H_{12}O_3NSNa \cdot 2H_2O$ requires $H_2O = 11.2$ per cent. Found: S = 11.3; Na = 8.02. $C_{13}H_{12}O_3NSNa$ requires S = 11.22; Na = 8.07 per cent.).

Silver Salt. $CH_3N(C_6H_5) \cdot C_6H_4SO_3Ag$.—This was obtained in small colourless plates on mixing cold aqueous solutions of the pure sodium salt and pure silver nitrate (Found: Ag = 29.0. $C_{13}H_{12}O_3NSAg$ requires Ag = 29.10 per cent.).

The *barium salt*, $[CH_3N(C_6H_5) \cdot C_6H_4SO_3]_2Ba$, is very sparingly soluble in cold water and separates in beautiful, glistening plates on mixing boiling aqueous solutions of the pure sodium salt and pure barium chloride (Found: Ba = 20.3. $C_{26}H_{24}O_6N_2S_2Ba$ requires Ba = 20.76 per cent.).

The *magnesium salt*, $[CH_3N(C_6H_5) \cdot C_6H_4SO_3]_2Mg \cdot 6H_2O$, has a much greater solubility in water than the barium salt and is very similar in appearance. It was prepared in a similar manner, using

magnesium sulphate (Found: $\text{H}_2\text{O} = 16.9$. $\text{C}_{26}\text{H}_{24}\text{O}_6\text{N}_2\text{S}_2\text{Mg} \cdot 6\text{H}_2\text{O}$ requires $\text{H}_2\text{O} = 16.5$ per cent. Found: $\text{Mg} = 4.03$. $\text{C}_{26}\text{H}_{24}\text{O}_6\text{N}_2\text{S}_2\text{Mg}$ requires $\text{Mg} = 4.43$ per cent.).

The free acid prepared from the pure barium salt by treatment with the calculated quantity of sulphuric acid did not crystallise on being left in a vacuum desiccator for some weeks. After unsuccessful attempts to prepare the acid chloride and definite nitration products, it was converted into the aniline salt.

Aniline Salt, $\text{CH}_3 \cdot \text{N}(\text{C}_6\text{H}_5) \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_3\text{NH}_3 \cdot \text{C}_6\text{H}_5$.—This was prepared by carefully mixing the free acid with a slight excess of pure aniline. The salt may be recrystallised from alcohol, in which it is readily soluble, but it is best separated from any aniline sulphate, the presence of which may be due to a little free sulphuric acid in the crude methyldiphenylaminesulphonic acid, by recrystallisation from moist benzene. From this solvent the salt separates in fine, colourless needles which rapidly effloresce in air. The salt may be further purified by recrystallisation from boiling water and dried at the ordinary temperature (Found: $\text{C} = 64.3$; $\text{H} = 5.70$. $\text{C}_{19}\text{H}_{20}\text{O}_3\text{N}_2\text{S}$ requires $\text{C} = 64.00$; $\text{H} = 5.66$ per cent.).

On heating in a melting-point tube, the aniline salt melts sharply at 179 – 180° (uncorr.), and on further heating the product in the tube resolidifies at 195 – 196° . This is the only derivative of the acid so far described which has a definite melting point and is therefore convenient for the identification of the acid.

For the investigation of the action of heat, 4.3 grams of the pure aniline salt were heated in a gentle stream of dry carbon dioxide. The temperature of the heating bath was gradually raised to and finally maintained at 210 – 215° for one hour. Drops of an oily liquid appeared on the sides of the tube after the contents had melted and solidified. After washing and drying, the solid product weighed 2.15 grams. It was recrystallised from water and obtained in colourless, tabular crystals which contained water of crystallisation. The substance had the physical and chemical properties of sulphanilic acid, and its identity was finally fully established by the analysis of the pure anhydrous material (Found: $\text{C} = 41.2$, 41.4 ; $\text{H} = 4.1$, 4.1 . Calc., $\text{C} = 41.58$; $\text{H} = 4.08$ per cent.). Sulphanilic acid was also produced when the aniline salt was boiled with an excess of aniline. The benzene washings from the sulphanilic acid, on evaporation, gave a liquid residue, somewhat blue in colour, which was basic and had the characteristic odour of methyldiphenylamine. This was converted into the chloroplatinate (Found: $\text{Pt} = 24.4$. Calc., $\text{Pt} = 25.15$ per cent.). Although the salt was apparently not quite pure, it is evident that the oil from which it was produced was chiefly methyldiphenylamine.

According to the equation $\text{CH}_3\cdot\text{N}(\text{C}_6\text{H}_5)\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3\text{NH}_2\cdot\text{C}_6\text{H}_5 = \text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3\text{H} + \text{CH}_3\cdot\text{N}(\text{C}_6\text{H}_5)_2$, 2.09 grams of anhydrous sulph-anilic acid should be obtained from 4.3 grams of the aniline salt, whereas 2.15 grams was the weight of the crude dry material actually obtained.

When 31 grams of methyldiphenylamine were heated with 17 grams of concentrated sulphuric acid under the conditions described by Cloëz (*loc. cit.*), 11.9 grams of unchanged base were recovered and 12 grams of a crude sodium methyldiphenylaminesulphonate obtained. This crude salt shows a marked tendency to become blue and is evidently a somewhat complex mixture. On careful crystallisation, only 6 grams of pure sodium methyldiphenylaminesulphonate, identical with the salt already described, were obtained (Found : $\text{H}_2\text{O} = 11.5$. $\text{C}_{13}\text{H}_{12}\text{O}_3\text{NSNa}\cdot 2\text{H}_2\text{O}$ requires $\text{H}_2\text{O} = 11.2$ per cent. Found : $\text{Na} = 7.9$. $\text{C}_{13}\text{H}_{12}\text{O}_3\text{NSNa}$ requires $\text{Na} = 8.07$ per cent.). The identity of the salt was finally established by conversion into the barium salt, free acid, and finally into the aniline salt, which melted at $179-180^\circ$ and the molten product resolidified at $195-196^\circ$. A mixture with the aniline salt previously described showed no difference in behaviour.

The best way of preparing sodium methyldiphenylamine-sulphonate is by the action of methyl sulphate on methyldiphenylamine, which reaction, according to Gadomska and Decker (*loc. cit.*), only gives rise to a salt of diphenyldimethylammonium hydroxide. The following is a description of a typical preparation.

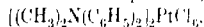
A mixture of 39.2 grams (1 mol.) of methyldiphenylamine and 27 grams (1 mol.) of methyl sulphate was heated on the water-bath for twelve hours, dimethyl ether being produced during the reaction. The product was boiled with an aqueous solution of sodium hydroxide for two hours and then extracted with benzene at about 50° . After drying, the benzene extract was distilled and gave 12.9 grams of methyldiphenylamine, b. p. $290-295^\circ$. Sodium methyldiphenylaminesulphonate separated in the characteristic manner from the aqueous alkaline solution. It weighed 22.8 grams, corresponding to a yield of 55.7 per cent., calculated on the amount of base used up in the reaction, and after one recrystallisation from 90 per cent. alcohol it was found to be pure. It was dried at 110° (Found : $\text{Na} = 7.8$. Calc., $\text{Na} = 8.07$ per cent.). By conversion into the aniline salt it was shown to be identical with the sodium salt already described.

Salts of Diphenyldimethylammonium Hydroxide.

The formation of a heavy oil on working up the product of the methylation of diphenylamine under the conditions described by

Ullmann has already been referred to (p. 834). For the preparation of a sufficient quantity for investigation, 33.8 grams (1 mol.) of diphenylamine, 37.8 grams (1.5 mols.) of methyl sulphate, and 50 c.c. of benzene were heated for six hours on the water-bath. The product was then mixed in the cold with a slight excess of sodium hydroxide solution and the heavy oil which separated at the bottom of the solution was removed. Sodium methyldiphenylamine-sulphonate crystallised as usual from the alkaline solution and methyldiphenylamine and unchanged diphenylamine were separated from the benzene layer. The oil is readily soluble in water and separates again from its aqueous solution on addition of alkali. The oil is also soluble in alcohol and from the alcoholic solution sodium methyldiphenylaminesulphonate (identified by analysis) separated, showing that the latter compound is soluble in the oil. That the oil consisted chiefly of diphenyldimethylammonium hydroxide was shown by the preparation from it of the chloroplatinate, iodide, and picrate.

Diphenyldimethylammonium chloroplatinate,



which has not been previously described, was obtained as a golden-yellow precipitate from the oil in the usual manner. It decomposes at 180–182° (Found: Pt = 23.7. $\text{C}_{28}\text{H}_{32}\text{N}_2\text{Cl}_6\text{Pt}$ requires Pt = 24.3 per cent.).

The iodide of the same base was prepared by the addition of concentrated aqueous hydriodic acid to the alcoholic solution of the oil. Its separation in colourless needles was facilitated by the addition of ether. The salt was recrystallised from alcohol, and by its melting point (163–164°) and analysis (Found: I = 39.3. Calc., I = 39.05 per cent.) was proved to be identical with the compound prepared by Gadouska and Decker by the action of potassium iodide on the corresponding methosulphate. The picrate, prepared from the alcoholic solution of the oil in the usual manner, separated in beautiful yellow plates melting at 167–168°.

The following experiment illustrates the most convenient method for the preparation of diphenyldimethylammonium iodide. 24.4 Grams (1 mol.) of methyldiphenylamine, 16.8 grams (1 mol.) of methyl sulphate, and 30 c.c. of benzene were heated for twelve hours on the water-bath. The reaction product was shaken with a saturated aqueous solution of 28 grams of potassium iodide. The colourless crystals which separated were filtered off and after drying weighed 12.2 grams, that is, 28.1 per cent. of the theoretical quantity. They were recrystallised from alcohol and had a melting point of 166–168°, and were therefore diphenyldimethylammonium iodide. The filtrate from the iodide was made alkaline with a slight excess

of a solution of sodium hydroxide, steam-distilled to remove the benzene, and then boiled for thirty minutes. From the alkaline solution, 4.8 grams of methyldiphenylamine (19.7 per cent. of the theoretical quantity) were recovered by extraction with benzene, and 13.2 grams of sodium methyldiphenylaminesulphonate (34.7 per cent. of the theoretical quantity) were filtered off. The latter compound was recrystallised from 90 per cent. alcohol and proved to be identical with the sodium salt described above. When the product of the reaction is worked up in the reverse order, that is, by treatment first with sodium hydroxide and then with potassium iodide, a larger quantity, amounting on the average to 45.9 per cent. of the theoretical quantity, of methyldiphenylamine is recovered, whilst the iodide tends to be contaminated with the sodium salt of methyldiphenylaminesulphonic acid. The larger amount of methyldiphenylamine obtained in this case shows that the quaternary hydroxide is to some extent decomposed by boiling the alkaline solution.

The same quantities of methyldiphenylamine and methyl sulphate were heated at 140–150° for two hours, that is, under the conditions described by Gadomska and Decker (*loc. cit.*). At 130–135°, a very vigorous reaction, which very quickly subsided, set in and volatile products (probably dimethyl ether and methyl alcohol) were evolved. The reaction product was worked up in a manner similar to that described above: 11.8 grams of diphenyldimethylammonium iodide (m. p. 166–168°), that is, 27.2 per cent. of the theoretical quantity, 12.0 grams of sodium methyldiphenylaminesulphonate (31.6 per cent. of the theoretical quantity), and only a small amount of unchanged methyldiphenylamine were obtained.

Action of Ethyl Sulphate on Diphenylamine. Ethyldiphenylamine.

The ethyl sulphate used was neutral in reaction and boiled at 89–92°/12 mm. The reaction was carried out under the same conditions as for the preparation of methyldiphenylamine (p. 834) except that the time of heating was twenty hours. During the reaction diethyl ether was detected in the flask, and the mixture finally became green and highly viscous. The product was worked up in the usual manner. No very definite indication of the formation of a sulphonic acid of ethyldiphenylamine was obtained. From 33.8 grams (1 mol.) of diphenylamine and 46.2 grams (1.5 mols.) of ethyl sulphate, 15.4 grams (39.0 per cent. calculated on the diphenylamine taken) of ethyldiphenylamine and 2.9 grams of diphenylamine hydrochloride were obtained. When the time of heating was twelve hours, a yield of 35.5 per cent. of ethyldiphenylamine was obtained.

The crude ethyldiphenylamine boiled at 292–295°. As some uncertainty exists with regard to the boiling point of ethyldiphenylamine, the product was carefully purified by distillation. The pure base, which is an almost colourless oil, has a boiling point of 149·5–150°/10 mm. It was identified by conversion in the usual manner into its chloroplatinate, which does not appear to have been previously described. This compound was obtained in golden-yellow prisms, m. p. 166–169° with decomposition (Found: Pt = 23·9. $C_{28}H_{32}N_2Cl_6Pt$ requires Pt = 24·27 per cent.).

We desire to express our thanks to Mr. F. B. Windle for his help in connexion with the analytical portion of this work.

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[Received, February 1st, 1923.]

CL.—*The Properties of Ammonium Nitrate. Part V. The Reciprocal Salt-pair, Ammonium Nitrate and Potassium Chloride.*

By EDGAR PHILIP PERMAN and HORACE LEONARD SAUNDERS.

THIS system is similar in many respects to that of ammonium nitrate and sodium chloride, dealt with in Part IV. The chief difference is that in this case the two nitrates are isomorphous whereas there is no isomorphism between sodium and ammonium nitrates.

The method employed was the same as described in Part III (T., 1922, 121, 963) with the exception that a sharper reading of the crystallising point was obtained by placing a metal filament electric lamp behind the tube containing the fused salt. When crystallisation began, two adjacent filaments could no longer be distinguished. In this way, a difference of no more than 0·2° in consecutive readings was obtained.

Binary Systems. There are five, namely:

(a) Ammonium nitrate and ammonium chloride (see Part IV, T., 1922, 121, 2475). Eutectic temperature at 141°.

(b) Ammonium nitrate and potassium nitrate. Eutectic temperature at 156·5° with 13·6 per cent. of KNO_3 .

(c) Potassium nitrate and potassium chloride. Eutectic temperature at 331·5° with 5·6 per cent. of KCl.

(d) Ammonium chloride and potassium chloride: cannot be realised.

(e) In addition to these, the general diagram shows that ammonium

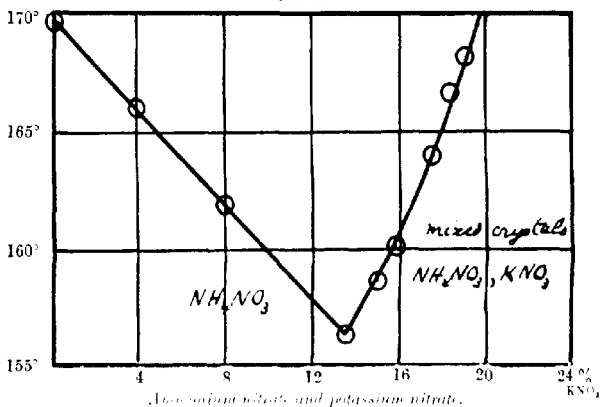
chloride can form a binary system together with mixed crystals of ammonium and potassium nitrates.

Ternary Systems.—Only one has been realised, namely, ammonium chloride, ammonium nitrate, and mixed crystals of potassium nitrate and ammonium nitrate (together with liquid and vapour) at a temperature of 134.5° ; but for the decomposition of the ammonium salts, another system would be expected, consisting of ammonium chloride, potassium chloride, and mixed crystals of potassium nitrate and ammonium nitrate.

Melting-point curves have been constructed for the following mixtures, with varying proportions of the constituents :

(1) Ammonium nitrate and ammonium chloride. (2) Ammonium nitrate and potassium nitrate. (3) Ammonium nitrate and potass-

FIG. 1.



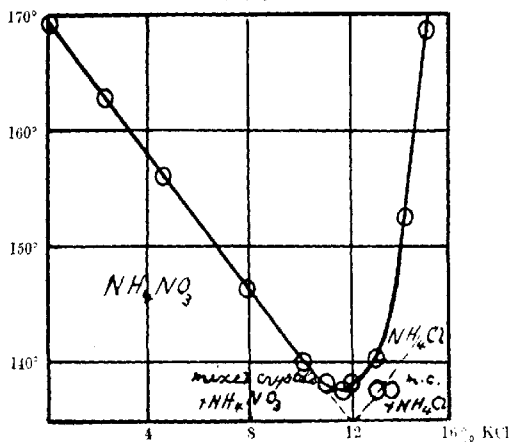
ium chloride. (4) (Ammonium nitrate + 1.87 per cent. of ammonium chloride) and potassium chloride. (5) (Ammonium nitrate + 4 per cent. of ammonium chloride) and potassium chloride. (6) (Ammonium nitrate + 7 per cent. of ammonium chloride) and potassium chloride. (7) (Ammonium nitrate + 9.5 per cent. of ammonium chloride) and potassium chloride. (8) (Ammonium nitrate-ammonium chloride eutectic) and potassium chloride. (9) (Ammonium nitrate-ammonium chloride eutectic) and potassium nitrate. (10) (Ammonium nitrate + 4 per cent. of potassium nitrate) and potassium chloride. (11) (Ammonium nitrate + 8 per cent. of potassium nitrate) and potassium chloride. (12) (Ammonium nitrate + 10 per cent. of ammonium chloride) and potassium nitrate. (13) (Ammonium nitrate + 13.6 per cent. of potassium nitrate) and potassium

chloride. (14) (Ammonium nitrate-potassium nitrate eutectic) and ammonium chloride. (15) (Ammonium nitrate + 16 per cent. of potassium nitrate) and ammonium chloride. (16) (Ammonium nitrate + 19 per cent. of potassium nitrate) and ammonium chloride. (17) Potassium nitrate and potassium chloride.

Curve 1. Ammonium Nitrate and Ammonium Chloride (loc. cit.).

Curve 2. Ammonium Nitrate and Potassium Nitrate (Fig. 1).— Although these salts are isomorphous, the curve shows a well-defined minimum and is of the usual type for two substances forming neither a compound nor mixed crystals. However, a few similar cases have been observed previously, namely, naphthalene

FIG. 2.



Ammonium nitrate and potassium chloride.

and monochloroacetic acid, potassium and thallium nitrates (Cady, *J. Physical Chem.*, 1899, 3, 127; Van Eyk, *Z. physikal. Chem.*, 1899, 30, 430). The crystals are well defined on both sides of the minimum and very similar to each other. By analysis, the crystals separating have been shown to be ammonium nitrate below 13.6 per cent. of potassium nitrate, and a little above that concentration mixed crystals of the two nitrates with about 45 per cent. of the potassium salt.

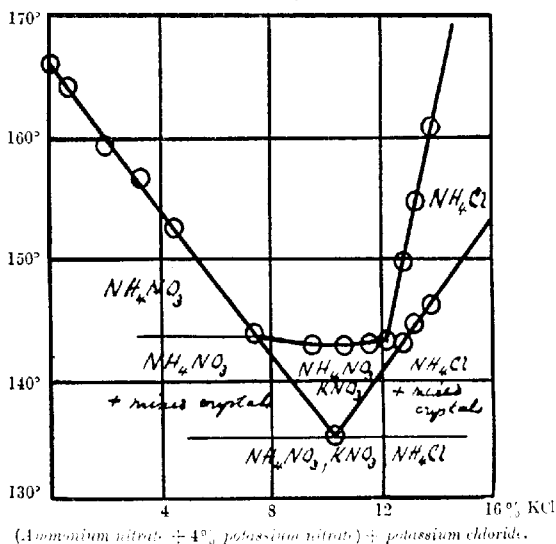
This proportion would no doubt increase with increase of potassium nitrate in the *liquides*, until the temperature became unworkable.

Curve 3. Ammonium Nitrate and Potassium Chloride.—This is a ternary system, and the curve (Fig. 2) is typical of several others,

for example, curves 4, 15, 16. It consists of two straight branches connected by a curved portion. The crystals separating are as shown in the diagram; below the straight branches, ammonium nitrate and ammonium chloride, respectively; below the curved portion, mixed crystals; on either side of this area, mixed crystals are added to the salt separating higher up.

Curves 5, 6, and 7 (ammonium nitrate, ammonium chloride, and potassium chloride) each consist of two straight branches, ammonium nitrate crystallising on one side, and ammonium chloride on the

FIG. 3.



other. The lowest point of curve 5 is the lowest temperature (134.5°) obtained in the series and represents the ternary eutectic ammonium nitrate, ammonium chloride, and mixed crystals. It is confirmed by several secondary arrests (see appendix). Curves 6 and 7 are similar except that at and below the lowest point the solid phase consists of ammonium nitrate and ammonium chloride.

Curve 8 is without a left branch. There are several secondary arrests following the binary eutectic curve (see general diagram).

Curve 9 (ammonium nitrate-ammonium chloride eutectic and potassium nitrate) first falls and then rises; it is almost entirely in the ammonium chloride area throughout. Below it is a somewhat

similar curve of secondary arrests following the binary curves ammonium nitrate, ammonium chloride, and later mixed crystals ($\text{AmNO}_3, \text{KNO}_3$) and ammonium chloride (see general diagram).

Curves 10 and 11 (ammonium nitrate + 4 per cent. (8 per cent.) of potassium nitrate and potassium chloride) are of an exceptional character and consist of straight branches (the right-hand one being very steep), joined below by a short curve which is nearly horizontal (Fig. 3). The solid phases are as shown in the diagram.

The mixed crystal area is a small triangular space below the flat curve.

Secondary arrests corresponding with the binary eutectics converge to the ternary eutectic at 134.5° .

Curve 12 (Ammonium Nitrate + 10 per cent. of Ammonium Chloride) and Potassium Nitrate.—Left branch straight; right branch gently curved, solid phase mixed crystals.

Curve 13 (Ammonium Nitrate + 13.6 per cent. of Potassium Nitrate) and Potassium Chloride.—Flat curve entirely in the mixed crystal area.

Curve 14 (ammonium nitrate and potassium nitrate eutectic) and ammonium chloride, passes through the ternary eutectic; which is confirmed by several secondary arrests. Left branch straight, solid phase ammonium nitrate; right branch slightly curved, solid phase ammonium chloride.

Curve 15 (ammonium nitrate + 16 per cent. of potassium nitrate) and ammonium chloride, consists of two straight, or nearly straight branches connected by a curved portion below. Solid phase on left side, mixed crystals; on right side, ammonium chloride. There are some secondary arrests at the ternary eutectic temperature.

Curve 16 is similar to 15.

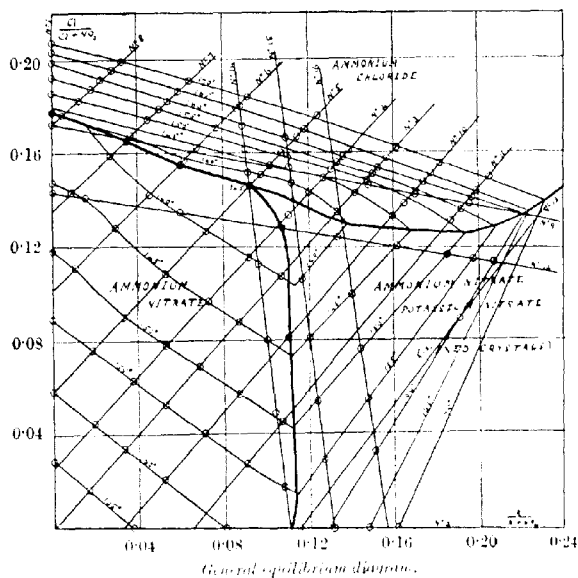
Curve 17 is of the usual two-branch type. (We are indebted to Mr. W. R. Harrison for this piece of work, which was carried out with a mercury thermometer. No great accuracy can be claimed owing to the length of the exposed stem.)

General Diagram. The whole of the results are embodied in a general diagram (Fig. 4), constructed as described in Part IV (*loc. cit.*, p. 247). It shows one ternary system, namely, ammonium nitrate, ammonium chloride, and mixed crystals (AmNO_3 and KNO_3) in equilibrium, together with liquid and vapour, at 134.5° . Three binary systems are shown, already described, p. 841: of the other two binary systems, only one has been realised, namely, potassium nitrate and potassium chloride with a eutectic at 334.5° . To complete the diagram there should be evidently another ternary system consisting of potassium chloride, ammonium chloride, and mixed crystals (AmNO_3 and KNO_3), but it has not been found

possible to realise it owing to the decomposition of the ammonium salts.

A noteworthy feature of this diagram is the flatness of the mixed crystal area.

FIG. 4.



Summary.

- (1) The freezing point of ammonium nitrate is lowered from 169° to 156.5° by the addition of potassium nitrate, mixed crystals of the two salts separating at that temperature.
- (2) By the addition of ammonium chloride and potassium nitrate to ammonium nitrate the freezing point is lowered to 134.5° .
- (3) An equilibrium diagram is given for the system



It shows a ternary eutectic at 134.5° for ammonium nitrate, ammonium chloride, and mixed crystals of potassium and ammonium nitrates.

- (4) There is probably another ternary point, not realisable at ordinary pressures.

- (5) When an isomorphous mixture (or mixed crystals) forms a

definite eutectic, the character of the equilibrium system appears to be the same as when no isomorphous mixtures are present.

The whole of the experimental results are given in the following appendix.

APPENDIX.

Freezing Points of Binary Mixtures.

Curve (1). Addition of NH_4Cl to NH_4NO_3 .

0% NH_4Cl	0.0	1.78	4.0	7.0	9.5
F , pt.	169.6°	165.3°	159.3°	152.8°	147.2°
0% NH_4Cl	10.0	12.1	13.32	14.41	15.54
F , pt.	146.3	141.7	136.3	132.0	127.5

(2) Addition of KNO_3 to NH_4NO_3 (Fig. 1).

0% NH_4NO_3	0.0	4.0	8.0	13.4	16.0
F , pt.	169.5°	166.6	162.8	157.3	160.1°
0% NH_4NO_3	19.0	15.0	15.88	17.49	18.3
F , pt.	167.9°	158.6	160.0	164.0°	165.9°

Freezing Points of Ternary Mixtures.

(3) Addition of KCl to NH_4NO_3 (Fig. 2).

0% KCl	0.0	2.34	4.43	8.0	10.0	10.5	11.07
F , pt.	169.6	162.7	155.9	146.6	139.8	138.8	137.9°
Arrest							137.8°
0% KCl	11.2	12.36	13.0	13.15	13.6	14.13	15.1
F , pt.	137.3	137.0	137.5	140.0	147.2	152.2	168.0
Arrest			137.2	137.2	137.3	137.0	

(4) Addition of KCl to $(\text{NH}_4\text{NO}_3 + 1.78\% \text{NH}_4\text{Cl})$.

0% KCl	0.0	3.22	6.25	9.08	10.45	
F , pt.	165.3	155.7	147.1	138.1	134.7	
0% KCl	11.0	11.78	12.0	12.6	12.8	13.1
F , pt.	134.4	142.1	146.7	155.0	157.5	165.7
Arrest		134.7	134.7	137.0	137.9	139.4

(5) Addition of KCl to $(\text{NH}_4\text{NO}_3 + 4\% \text{NH}_4\text{Cl})$.

0% KCl	0.0	3.22	4.77	6.26	7.7
F , pt.	159.3	150.0	146.1	140.0	137.2
0% KCl	8.8	9.1	9.8	11.0	11.8
F , pt.	135.1	137.4	145.2	160.1	168.0
Arrest	134.8		134.2	134.5	

(6) Addition of KCl to $(\text{NH}_4\text{NO}_3 + 7\% \text{NH}_4\text{Cl})$.

0% KCl	0.0	2.45	3.60	4.76	5.88
F , pt.	152.8	146.3	142.9	139.5	137.1
0% KCl	6.78	7.7	8.46	9.3	
F , pt.	146.6	158.1	166.8	177.0°	
Arrest	136.6°	137.0	136.8	135.4°	

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(7) Addition of KCl to $(\text{NH}_4\text{NO}_3 + 9.5\% \text{NH}_4\text{Cl})$.

% KCl	0.0	1.0	1.96	2.9	3.84
F. pt.	147.2°	144.5°	142.0°	139.6°	144.8°
Arrest					138.8°
% KCl	4.3	4.76	5.2	5.65	
F. pt.	148.2°	155.5°	158.7°	165.5°	
Arrest	137.2°	138.2°	138.2°	137.4°	

(8) Addition of KCl to $(\text{NH}_4\text{NO}_3 + 12.1\% \text{NH}_4\text{Cl})$ (eutectic).

% KCl	0.0	0.99	1.96	2.9	3.85
F. pt.	141.1°	145.9°	154.6°	165.0°	173.7°
Arrest		141°	140°	138.4	137.4°

(9) Addition of KNO_3 to $(\text{NH}_4\text{NO}_3 + 12.1\% \text{NH}_4\text{Cl})$.

% KNO_3	0.0	4.76	6.98	11.1	14.9
F. pt.	141.1°	138.0°	139.0°	142.7°	146.6°
Arrest			136.8	134.5°	134.0°
% KNO_3	16.7	18.4	20.0	23.1	25.0
F. pt.	147.5°	149.2	151.8°	156.8	160.8°
Arrest	136.6	139.7°	142.0°	146.2°	152.8

(10) Addition of KCl to $(\text{NH}_4\text{NO}_3 + 4\% \text{KNO}_3)$.

% KCl	0.0	0.66	1.96	3.22	4.45	7.4
F. pt.	166.0	164.2	159.4	156.9°	152.7°	143.9°
% KCl	10.3	10.7	11.78	12.25	12.8	13.3
F. pt.	142.9°	142.6°	142.9	143.0	149.7	151.4
Arrest	134.9			142.9	143.9	144.7°

(11) Addition of KCl to $(\text{NH}_4\text{NO}_3 + 8\% \text{KNO}_3)$.

% KCl	0.0	1.45	4.58	5.78	6.96	8.1	8.8
F. pt.	162.8°	158.3	149.1	148.6	148.1°	147.7	147.6
Arrest				145.4°	140.3°		135.3°
% KCl	9.21	11.0	11.8	11.9	12.28	13.08	13.9
F. pt.	147.8	148.0	148.3	149.4	151.6°	158.7	160.0
Arrest			147.5	147.4	148.0	150.5	

(12) Addition of KNO_3 to $(\text{NH}_4\text{NO}_3 + 10\% \text{NH}_4\text{Cl})$.

% KNO_3	0.0	3.22	6.25	9.1	11.77	14.27
F. pt.	146.3°	144.1	141.9	139.4	137.2	135.8
% KNO_3	16.66	18.9	21.09	25.0	27.6	
F. pt.	139.4	142.9	146.4	157.8	168.5	

(13) Addition of KCl to $(\text{NH}_4\text{NO}_3 + 13.6\% \text{KNO}_3)$.

% KCl	0.0	0.99	2.11	4.75	5.95
F. pt.	158.9	156.9	156.3°	155.6	157.9°
% KCl	6.97	7.0	8.0	9.0	
F. pt.	157.9	158.0	158.9	162.9°	

(14) Addition of NH_4Cl to $(\text{NH}_4\text{NO}_3 + 13.6\% \text{KNO}_3)$ (eutectic).

% NH_4Cl	0.0	1.48	2.92	5.21	7.4
F. pt.	157.3	153.0	149.8	143.7°	139.6
% NH_4Cl	9.5	10.3	11.1	11.5	
F. pt.	134.5	139.8	149.5	154.9°	
Arrest		134.2°	134.5	134.2	

(15) Addition of NH_4Cl to $(\text{NH}_4\text{NO}_3 + 16\% \text{KNO}_3)$.

% NH_4Cl	0.0	2.38	3.66	5.36	6.08	
F. pt.	160.0°	153.4°	149.7°	144.4°	143.0°	
% NH_4Cl	8.28	8.81	10.0	11.0	11.54	12.06
F. pt.	136.8°	135.9°	143.6°	150.6°	161.9°	166.2°
Arrest	134.5°	135.0°	134.8°			

 (16) Addition of NH_4Cl to $(\text{NH}_4\text{NO}_3 + 19\% \text{KNO}_3)$.

% NH_4Cl	0.0	0.99	2.66	4.15	4.52
F. pt.	167.9°	164.8°	157.0°	152.0°	151.9°
% NH_4Cl	5.65	6.83	7.98	8.55	9.64
F. pt.	147.9°	143.8°	141.7°	142.8°	145.9°
Arrest			134.9°	135.1°	

 (17) Binary system not appearing in the general diagram. Addition of KCl to KNO_3 .

% KCl ...	0.0	1.05	2.34	4.67	6.86	7.88	10.12	12.45
F. pt. ...	344°	343°	341°	336°	339°	345°	357°	371°

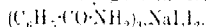
UNIVERSITY COLLEGE, CARDIFF.

[Received, February 9th, 1923.]

CII.—Preparation of Potassium and Sodium Arylsulphoniodamides.

By ELWYN ROBERTS.

IN an attempt to prepare benzioidamide, $\text{C}_6\text{H}_5\cdot\text{CO}\cdot\text{NHI}$, by acidifying a solution of iodine and benzamide in caustic soda, Moore and Thomas (*J. Amer. Chem. Soc.*, 1914, **36**, 1928) obtained a coloured periodide to which they gave the formula



Similar periodides are, I find, obtained as dark, crystalline solids from benzene- and *p*-toluene-sulphonamides when a concentrated solution of iodine in aqueous potassium iodide is added to their aqueous alkaline solution. On the other hand, *o*-toluene-sulphonamide yields a pale yellow, crystalline solid, which is potassium toluene-*o*-sulphoniodamide, $(\text{CH}_3\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\cdot\text{NIK})_2\cdot\text{H}_2\text{O}$. This compound is the first salt of an iodoamide to be isolated, and is the iodine analogue of the bromo- and chloro-amides, of which the first was Hofmann's (*Ber.*, 1882, **15**, 40) acetobromoamide. In particular, the more closely analogous sulphonchloro- and sulphonbromo-amides have been prepared by Chattaway (F., 1905, **87**, 145 *et seq.*), and Dakin, Cohen, Daufresne, and Kenyon (*Proc. Roy. Soc.*, 1916, **89**, [B], 238).

The essential conditions for obtaining these iodoamide salts are the presence of hypoiodite and a high concentration of potassium or sodium, preferably as hydroxide, to reduce the solubility of these highly soluble salts.

Method 1.—A solution of the sulphonamide (4.5 grams) in the minimum quantity of 10 per cent. caustic potash (or caustic soda) is slowly added to a small excess of a solution of iodine in aqueous potassium or sodium iodide (9 grams of iodine and 18 grams of potassium or sodium iodide in 20 c.c. of water), whereupon, with the exception of *o*-toluene- and α -naphthalene-sulphonamides, periodides crystallise out. Fifty per cent. caustic potash (or 40 per cent. caustic soda) is introduced drop by drop, until the iodine and the periodide have disappeared. The salt of the sulphoniodoamide immediately separates as a yellow, crystalline powder; it is collected, quickly washed with a cold saturated solution of potassium (or sodium) chloride, pressed on porous tile, and dried in the air or over phosphoric oxide.

No separation of a salt of the iodoamide follows on the addition of an alkaline solution of the sulphonamide to a freshly prepared solution of iodine in concentrated caustic alkali; too little hypoiodite remains unchanged to permit the formation of the iodoamide (Taylor, T., 1900, 77, 725; Orton and Blackmann, *ibid.*, 830).

Method 2.—An alternative successful process is found in the addition drop by drop of 50 per cent. caustic potash (or 40 per cent. caustic soda) to an intimate mixture of iodine (2 grams, 25 per cent. excess) and sulphonamide (1 gram), covered with a few c.c. of water (2–4 c.c. for the more soluble, 10 c.c. for the less soluble iodoamides). The iodoamides are left as fine powders when the iodine has disappeared; periodides are obviously intermediately produced.

Acidification of the mother-liquors of the iodoamides, except *o*-toluene- and α -naphthalene-sulphoniodoamides, causes liberation of iodine and separation of periodides of the sulphonamides.

It was hoped that the use of the large quantities of potassium (or sodium) iodide, and of iodine might be avoided by the addition of a solution of iodine monochloride in hydrochloric acid to a solution of the sulphonamide in concentrated caustic alkali, since $\text{ICl} + 2\text{KOH} = \text{KIO} + \text{KCl} + \text{H}_2\text{O}$. The difficulties of mixing the components at the high concentrations which are required for the isolation of the salts were insuperable on the small scale. Iodine appeared, and the reaction represented by the above equation was only partly realised. There was no improvement in the yield of iodoamide calculated on the iodine used.

By the above methods, the potassium salts of benzene-, *o*- and *p*-toluene-, and α - and β -naphthalene-sulphoniodoamides have been prepared, but only the sodium salts, which are far more soluble, from *o*-toluene- and α -naphthalene-sulphonamides. The yield varies between 50 and 85 per cent. These salts have a pale

yellow colour, form pale yellow solutions, and decompose slowly when exposed to the air. They have the characteristic hypoiodite odour. The water of crystallisation is lost at 75°, or on keeping over phosphoric oxide. When heated, the solid "explodes" at temperatures varying with the salt and the rate of heating. The iodoamides cannot be recrystallised from water, in which medium they become, on warming, extensively hydrolysed; free iodine appears, and ultimately iodide, iodate, and the original sulphonamide are produced. At the ordinary temperature, the same decomposition occurs, but less rapidly; in the case of a 1 per cent. solution of potassium toluene-*o*-sulphoniodoamide, after one day, 35 per cent. of the salt has disappeared, but after six days 45 per cent. is still unchanged. This decomposition is greatly delayed in a dilute alkaline medium: thus, in the presence of one equivalent of alkali hydroxide or carbonate, 20 per cent. has decomposed in twenty-four hours, and 35 per cent. in six days. The solution behaves as a relatively stable hypoiodite; arsenite is oxidised rapidly and quantitatively, a reaction which serves for estimation; acetone and alcohol are converted into iodoform; with dilute aqueous ammonia, crystalline nitrogen iodide is formed; with aqueous methylamine, di-iodomethylamine is formed as microscopic dichromate-like crystals; phenols react readily, yielding iodo-derivatives. On acidification of the solution with acetic acid, iodine appears and the sulphonamide is precipitated. In this reaction the salts of sulphoniodoamides differ from those of the chloro- and bromo-amides, which yield the sulphonidihalogenoamides, ArSO_2XX_2 , on acidification.

Potassium and Sodium Arylsulphoniodoamides.

Potassium Benzenesulphoniodoamide, $\text{C}_6\text{H}_5\text{SO}_2\text{NIK}$ or $\text{C}_6\text{H}_5\text{SO}(\text{OK})\text{NI}$.

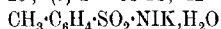
—This salt and those subsequently described were prepared by the two methods. Under (a), (b), the analyses of the compound prepared respectively by the first and second methods are given [Found: (a) I = 38.53; K = 13.09; (b) I = 43.01; K = 12.73. $\text{C}_6\text{H}_5\text{SO}_2\text{NIK}$ requires I = 39.51; K = 12.19 per cent.]. The salt when kept in a dry atmosphere and excluded from light, is nearly white.

*Potassium Toluene-*p*-sulphoniodoamide*, $\text{CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{NIK}$.

This compound is somewhat less soluble in water than the corresponding benzene compound [Found: (a) I = 36.15; K = 11.65; (b) I = 37.00; K = 12.20. $\text{CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{NIK}$ requires I = 37.86; K = 11.66 per cent.].

*Potassium toluene-*o*-sulphoniodoamide*, $\text{CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{NIK.H}_2\text{O}$,

is by far the least soluble of the series (4.80 grams in 100 c.c. of water at 10°) and can be dried in air without undergoing decomposition [Found: (a) $I = 35.62$; $K = 10.71$; in material dehydrated over phosphoric oxide, $I = 37.96$; after heating at 75° for half an hour, $I = 37.29$; (b) $I = 35.44$; $K = 10.96$.



requires $I = 35.93$; $K = 11.08$. $\text{CH}_3\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\cdot\text{NIK}$ requires $I = 37.86$; $K = 11.66$ per cent.].

Sodium toluene-o-sulphonidoamide, $\text{CH}_3\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\cdot\text{NINa}, 2(?)\text{H}_2\text{O}$, is far more soluble in water than the corresponding potassium salt, and was hence obtained only in an impure state [Found: (a) $I = 33.09$; $\text{Na} = 7.78$; after heating at 65° for one hour, $I = 37.42$; (b) $I = 36.21$; $\text{Na} = 6.69$. $\text{CH}_3\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\cdot\text{NINa}, \text{H}_2\text{O}$ requires $I = 37.65$; $\text{Na} = 6.82$. $\text{CH}_3\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\cdot\text{NINa}, 2\text{H}_2\text{O}$ requires $I = 35.75$; $\text{Na} = 6.48$ per cent.].

Potassium naphthalene- α -sulphonidoamide, $\text{C}_{10}\text{H}_7\cdot\text{SO}_2\cdot\text{NIK}, 2\text{H}_2\text{O}$ [Found: (a) $I = 31.06$; $K = 9.74$; (b) $I = 31.23$; $K = 10.29$. $\text{C}_{10}\text{H}_7\cdot\text{SO}_2\cdot\text{NIK}, 2\text{H}_2\text{O}$ requires $I = 31.17$; $K = 9.60$ per cent.].

Sodium Naphthalene- α -sulphonidoamide, $\text{C}_{10}\text{H}_7\cdot\text{SO}_2\cdot\text{NINa}, (?)\text{H}_2\text{O}$.—This very soluble salt was not obtained pure [Found: (a) $I = 29.22$; (b) $I = 31.37$; $\text{Na} = 6.08$. $\text{C}_{10}\text{H}_7\cdot\text{SO}_2\cdot\text{NINa}, 3\text{H}_2\text{O}$ requires $I = 31.02$; $\text{Na} = 5.62$ per cent.].

Potassium naphthalene- β -sulphonidoamide, $\text{C}_{10}\text{H}_7\cdot\text{SO}_2\cdot\text{NIK}, (?)\text{H}_2\text{O}$ [Found: (a) $I = 33.21$; $K = 10.07$; (b) $I = 33.02$; $K = 9.77$. $\text{C}_{10}\text{H}_7\cdot\text{SO}_2\cdot\text{NIK}, \text{H}_2\text{O}$ requires $I = 32.65$; $K = 10.06$. $\text{C}_{10}\text{H}_7\cdot\text{SO}_2\cdot\text{NIK}$ requires $I = 34.19$; $K = 10.53$ per cent.].

Periodides from Arylsulphonamides.

These periodides can be easily prepared by mixing alkaline solutions of the sulphonamides with concentrated solutions of iodine in aqueous potassium iodide. Three grams of the sulphonamide, dissolved in 60 c.c. of 2½ per cent. caustic potash, are added slowly to a solution made up from 9 grams of iodine, 18 grams of potassium iodide, and 60 c.c. of water. The mixture is filtered and set aside for twenty-four hours, when the periodide separates as very dark, lustrous, flat crystals. They are collected, washed with a very small quantity of water, and dried over sulphuric acid. The "total" iodine was estimated by the Carius method, and the "free" periodide iodine by titration with thiosulphate.

The approximate formulæ of the periodides isolated are as follows: $3\text{C}_6\text{H}_5\cdot\text{SO}_2\cdot\text{NH}_2\cdot\text{KI}, 2\text{I}_2$ [Found: $K = 2.95$, 3.27 (3.41); $S = 6.66$, 6.84 (8.40); I (total) = 50.05, 51.59 (55.43); I (free) = 40.79, 42.92 (44.34) per cent.]. $3(p\text{-})\text{C}_6\text{H}_4\cdot\text{SO}_2\cdot\text{NH}_2\cdot\text{KI}, 3\text{I}_2$ [Found: $K = 2.77$, 2.75 (2.73); $S = 7.36$ (6.70); I (total) =

59.47, 58.84 (61.91); I (free) = 52.16, 55.77 (53.08) per cent.]. The values in brackets are calculated values for the formulæ adopted. The results show that independent preparations of a periodide do not give the same analytical values.

I wish to express my thanks to Professor Orton, F.R.S., at whose suggestion this investigation was undertaken, for his guidance and criticism; also to the Department of Scientific and Industrial Research for a grant which has enabled me to carry out the work.

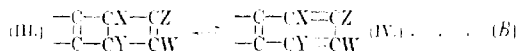
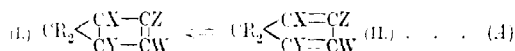
UNIVERSITY COLLEGE OF NORTH WALES,
BANGOR.

[Received, October 19th, 1922.]

CHH.—*The Chemistry of Polycyclic Structures in Relation to their Homocyclic Unsaturated Isomerides.*
Part IV. The Simulation of Benzenoid Properties by the Five-carbon Intra-annular Nucleus.

By CHRISTOPHER KELK INGOLD, ERNEST ARTHUR SEELEY, and
JOCELYN FIELD THORPE.

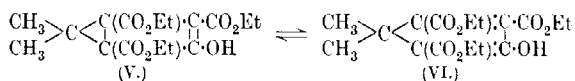
THE experiments described in the earlier parts of this series have led to the conclusion that in certain five-carbon nuclei there exists a condition of tautomerism characterised by reversible interchange between phases of the following general type (equation A), the individuals being related similarly to the Dewar and Kekulé phases of benzene (equation B):



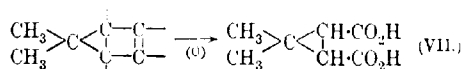
It will be recalled that part of the evidence cited (Ingold, T., 1922, 121, 1133) in favour of the view that the aromatic nucleus contains a system composed of bridged and Kekulé phases consists in the unification to which this view leads of the characteristic reactions of the aromatic series, for instance, the formation of ortho- and para-quinonoid structures by oxidative or additive reactions, migrations to the ortho- and para-positions, the substitution rather than the addition of halogens, and so forth. It is to be expected, therefore, that the five-carbon prototype (equation A) will, if the relative stability of the bridged and double-bonded phases sufficiently resembles that of the bridged and Kekulé phases of the benzene ring,

tend to simulate the truly aromatic type (equation *B*) in the possession of the characteristics mentioned; and the purpose of this paper is to show that it is possible so to adjust the stability of the phases in the five-carbon series that the compounds do actually simulate in a marked degree the properties of aromatic compounds.

Previous experiments (Farmer and Ingold, T., 1920, 117, 1362; Farmer, Ingold, and Thorpe, T., 1922, 121, 128) on the intramolecular tautomerism existing in five-carbon nuclei have largely been concerned with a series of substances derived from an acidic hydroxy-ester, all the observed transformations of which can be referred to one or other of the two formulæ (V) and (VI) :



From this parent substance a number of others were prepared, each of which was characterised by the possession of a two-fold series of properties, which, if considered as evidence of constitution, pointed with almost equal directness to two structures related to one another in the manner of formulæ (V) and (VI). The most striking feature of this series of substances was the remarkable stability of the bridged phase, which was such that it was possible, by careful attention to experimental conditions, to oxidise certain of the compounds to a *cyclopropane* acid (caronic acid, VII), the bridged linking surviving even although a considerable portion of the molecule was oxidised away :

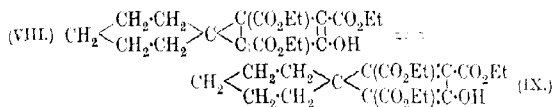


It is scarcely necessary to point out that this kind of reaction is quite unusual. A bridge bond, like a double bond, is an element of unsaturation, and, under normal conditions, is the point at which the attack of an oxidising agent commences. Hence it is that only in exceptional circumstances, in which the bridged phase is more than usually stable, is it possible to effect oxidative degradation in such a way that the bridge bond survives.

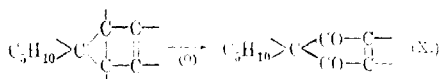
Therefore, for the purpose in view, it was necessary to adopt some means to reduce the stability of the bridged phase to the point at which, as in aromatic compounds, the attack of oxidising and other agents begins at the bridge; so that, in oxidation, for example, cyclic 1 : 4-diketones, analogous to para-quinones, would be the first isolable products.

The method which suggested itself for bringing about this result was to replace the *gem*-dimethyl group in the ester (V, VI) by

some more bulky grouping such as the methyl ethyl group or the residue of a *cyclohexane* ring; and at the commencement of our experiments evidence was already to hand which indicated *cyclohexane* derivatives as eminently suitable for the purpose; for it had previously been shown (Ingold and Thorpe, T., 1919, 115, 320) on theoretical grounds that the bridged linking in derivatives of the *cyclohexane-ester* (VIII) must be considerably weaker than that in the *gem*-dimethyl series, and the fact had been confirmed (Ingold and Thorpe, *loc. cit.*) as regards the stability of the bridge bond towards reducing agents by quantitative measurements,



The influence of the *cyclohexane* ring in diminishing the stability of the bridge bond to the point at which the condition of the structure has so far approached that of the aromatic nucleus as to give rise to a definite simulation in properties became evident from the outset of the investigation. Our first experiments had for their object to determine the behaviour of the structure on oxidative fission, and it was at once discovered that under conditions in which bridged compounds of the *gem*-dimethyl series yield the *cyclopropane* acid (VII) (caronic acid), that is, undergo oxidative fission in which the bridge bond is preserved intact, the corresponding *cyclohexane* substances give no trace of the analogous *spirocyclopropane* acid (XII) (a well-known and very stable acid), but in its place yield cyclic unsaturated 1:4-diketones of type (X), analogous in constitution to para-quinones:

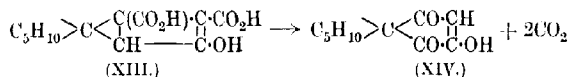


All attempts to isolate similar 1:4-diketones (XI) in the *gem*-dimethyl series have been fruitless, the sole product of oxidation of the bridged form being caronic acid (VII).



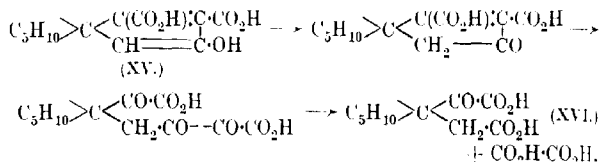
Thus in the *gem*-dimethyl series the dibasic acid corresponding with the acid (XIII) (below), on oxidation with alkaline ferricyanide, gave, in excellent yield, caronic acid accompanied by no other product (Farmer and Ingold, *loc. cit.*). On the other hand, the *cyclohexane* acid (XIII), on treatment with the same reagent, gave

a nearly quantitative yield of the cyclic 1:4-diketone (XIV) derived from the bridged phase (XIII) by the addition of oxygen at the bridge.



It is noteworthy that although these oxidations by ferricyanide take such different courses in the dimethyl and *cyclohexane* series, in neither case does the product contain any substance derived from the double-bonded phase of the original dibasic acid. Evidently in both series the double-bonded phases are stable to this particular reagent, the attack of which is directed, albeit in such different ways, against the bridged phases alone.

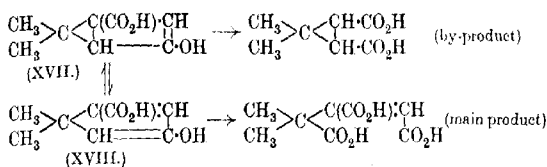
A similarly strong selective action is exerted by alkaline permanganate, which attacks only the double-bonded phase (XV) of the *cyclohexane* dibasic acid, yielding a cyclic ketoglutaric acid (XVI) and oxalic acid:



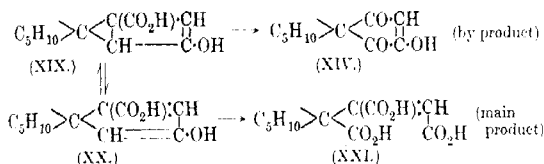
The reaction is exactly similar to the oxidation by permanganate of the corresponding *gem*-dimethyl acid, which yielded α -keto- β -dimethylglutaric acid and oxalic acid (*loc. cit.*).

Again, it should be noted that in neither series did the product contain any substance which could have been supposed to be produced by oxidative fission of the bridged phase of the original acid (Farmer, Ingold, and Thorpe, *loc. cit.*), whence it is evident that, in both series, alkaline permanganate, in contrast to ferricyanide, exerts a powerful selective action on the double-bonded phases.

A similar remarkable difference in the manner of oxidative fission of the bridged individual was observed in the case of the corresponding monobasic acid. It will be recalled that in the *gem*-dimethyl series ferricyanide attacked both the bridged and double-bonded forms, a small yield of caronic acid, derived from the bridged form (XVII), being accompanied by a large quantity of dimethylaconitic acid, the product of oxidation of the unsaturated isomeride (XVIII):

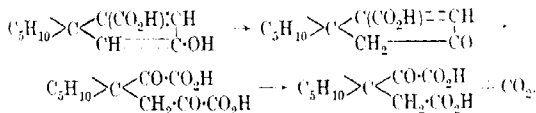


The *cyclohexane* acid, the two phases of which are shown by formulae (XIX) and (XX), also yielded two products, that present in largest amount being a cyclic aconitic acid (XXI) analogous to the dimethylaconitic acid (XVII). The by-product was, however, not the *cyclohexane* analogue of caronic acid, no trace of which was detected, but was the same quinone-like substance, which forms the sole product of oxidation of the dibasic acid under similar conditions:



These reactions are typical of a number described in this paper which show that quinone-like substances of the type (XIV) are the normal oxidation products of bridged modifications of this series of derivatives of the five-carbon monocyclic nucleus.

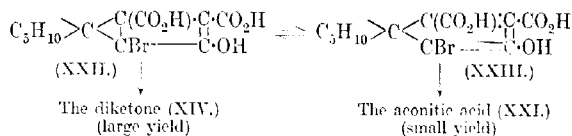
In the oxidation of the monobasic acid, permanganate again shows its selective action on the double-bonded phase, the ketonic acid (XVI) being the sole isolable product. The reaction is precisely similar to the oxidation by permanganate of the *gem*-dimethyl acid, which gives ketodimethylglutaric acid as the sole product:



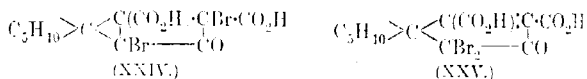
Another remarkable illustration of the analogy between the five-carbon nucleus and the fully aromatic type is to be found in the tendency of compounds of the former series to undergo substitution by halogens: the tendency is such that in every case hitherto investigated treatment with suitable quantities of halogen under almost any conditions leads to the successive and ultimately the complete replacement of all the nuclear hydrogen atoms, the

reaction taking place in every instance without the least sign of the formation of isolable additive products.

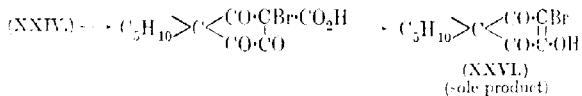
The formulæ (XIII) and (XV) for the dibasic acid show that in this substance there is only one nuclear hydrogen atom, namely, that in position 4. Treatment with two atoms of bromine, therefore, results in the introduction of a bromine atom into this position. The product is similar in all essential respects to the original acid, for instance in giving a yellow sodium compound and a strongly coloured iron salt, and the fact that it contains a similar intra-annular tautomeric system, represented by formulæ (XXII) and (XXIII), is shown by its oxidation with ferricyanide, the products of which are the "semi-quinone" (XIV) and a comparatively small amount of the aconitic acid (XXI) :



With the compound (XXII or XXIII), halogenation of the dibasic acid has reached a stage at which the only replaceable hydrogen atom is that on which the enolic properties of the substance depend; hence further substitution must be accompanied by ketonisation. The product of further bromination can therefore no longer contain an intra-annular tautomeric nucleus, and must be either a static bridged structure (XXIV) or a cyclic unsaturated compound (XXV) according as ketonisation takes place through form (XXII) or form (XXIII).



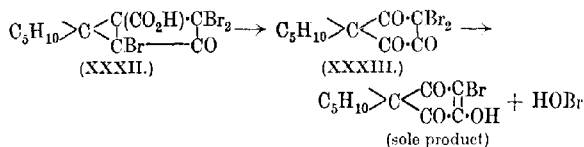
Experiment showed formula (XXIV) to be the correct one, for the substance on oxidation with ferricyanide yielded exclusively the bromo-derivative (XXVI) of the cyclic 1:4-diketone previously described :



No trace of an aconitic acid, suggesting the presence of the isomeride (XXV) could be detected.

This method of suppressing intra-annular tautomerism by en-

is so great that spontaneous reduction takes place in the presence of alkalis (Norris and Thorpe, T., 1921, 119, 1202) :

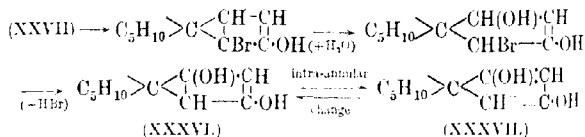


In the earlier communication dealing with the *gem*-dimethyl-dicyclopentane series, it was noted that certain halogen derivatives analogous to those described above can be converted by boiling alkalis into a remarkable series of substances, the dienolic forms of which (types XXXIV and XXXV) are analogous to resorcinol :

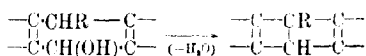


A number of substances of this type have now been obtained in the cyclohexanedicyclopentane series. Like phloroglucinol, they are partly ketonised, and although oximes have not been obtained, titration with bromine indicates a mono-enolic formula, whilst titration with alcoholic sodium ethoxide gives figures close to those required for a dihydric enol. All compounds of the series form coloured iron salts, yield dyes when coupled with diazotised aromatic bases in alkaline solution, and, indeed, exhibit remarkable similarity with their aromatic analogues.

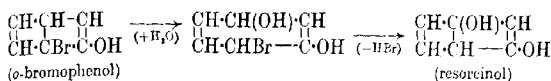
The modes of formation of these enols are of interest in so far as they involve the elimination of the elements of hydrogen bromide from the 1 : 4-positions of the ring, a type of transformation which is of extremely common occurrence in the aromatic series (Ingold, *loc. cit.*). The formation of the simplest of the enols (XXXVI or XXXVII) from the monobromo-monobasic acid (XXVII or XXXVIII) by boiling alkali must involve the following steps,



and may be likened to the formation of anthracene and its 9-alkyl-derivative from the hydroxy-dihydro-compounds :

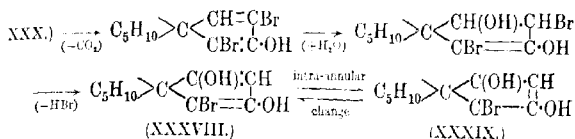


It also seems possible that the formation of resorcinol by the action of alkali at higher temperatures on ortho-derivatives of phenol or benzenesulphonic acid is due to an analogous transformation involving bridged modifications,

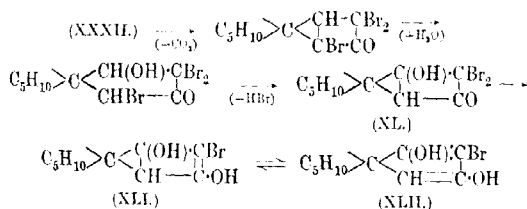


although the devising of a crucial experiment to test this view presents obvious difficulties.

The production of the bromo-enol (XXXVIII or XXXIX) from the dibromo-monobasic acid (XXIX or XXX) takes place evidently by way of the double-bonded modification of the nucleus, and to this extent resembles, perhaps, the formation of resorcinol from para-substituted phenols:

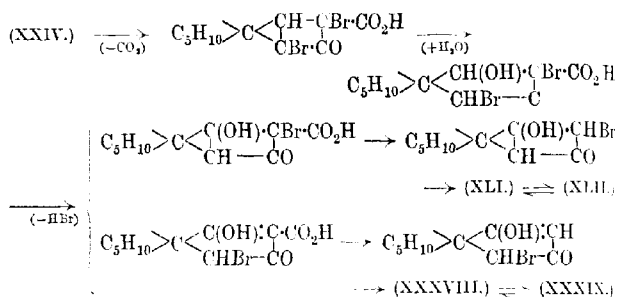


The isomeric bromo-enol (XLI or XLII) is obtained either by bromination of the enol (XXXVI or XXXVII) or by alkaline hydrolysis of the tribromo-monobasic acid (XXXII). This acid is a static bridged-ring keto-acid, and therefore it is to be expected that the course of its hydrolysis would be generally similar to that of the hydrolysis of the monobromo-acid, which, as shown above, reacts in its bridged modification. A consideration of the matter shows that the reaction very probably does take this course, and thereby gives rise to a substance (XL), the tendency of which to acquire the hydrogen atom necessary for tautomerism is such that spontaneous reduction occurs in the presence of the alkali, hypobromite being formed in the solution:

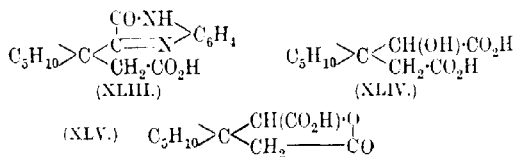


The alkaline hydrolysis of the monobromo-dibasic acid (XXII or XXIII) presents no point of special interest, the product and

probable course of the reaction being the same as in the case of the monobromo-monobasic acid. The dibromo-dibasic acid (XXIV), however, although it is a non-tautomeric bridged-ring compound, gave rise to a mixture of both the isomeric bromo-enols described above, and it is worthy of note that this observation falls well into line with the mechanism suggested for the whole series of hydrolytic transformations :

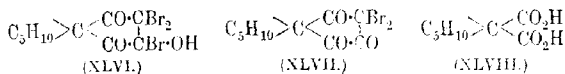


In conclusion, it should be said that the constitutions of the various oxidation and other products encountered in the course of this investigation were established by a close examination of their reactions and by converting them wherever possible into known substances. Thus the acid formulated as α -ketocyclohexane-1:1-diacetic acid (XVI) gave a condensation product (XLIII) with *o*-phenylenediamine (a property characteristic of α -ketonic acids), and on reduction by sodium amalgam yielded α -hydroxycyclohexane-1:1-diacetic acid (XLIV), the lactone of which (XLV) was identified by direct comparison, and by a determination of the mixed melting point, with a specimen which had been prepared at an earlier date by hydrolysis of the monobromination product of cyclohexane-1:1-diacetic acid (Beasley, Ingold, and Thorpe, T., 1915, 107, 1080) :

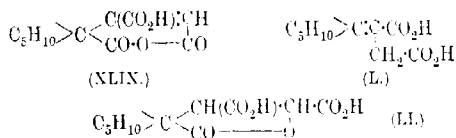


The cyclic diketone (XIV) was found to be mono-enolic, and owing presumably to its strongly acidic character it showed little tendency to combine with semicarbazide. It reduced alkaline

permanganate instantaneously and gave a bright cherry-red colour with ferric chloride. On bromination in the presence of water, it yielded the bromo-substitution product (XXVI), and with dry liquid bromine a dibromo-additive derivative (XLVI), which, on warming, lost hydrogen bromide, yielding the dibromo-ketone (XLVII). This substance, unlike the monobromo-substitution product (XXVI), was not an acid, but, on treatment with cold dilute alkalis, it yielded hypobromous acid and the monobromo-compound (compare p. 860). None of the compounds of the series showed any tendency to combine with water or to exhibit any other of the characteristic properties of 1:2:3-triketones, and all on oxidation by permanganate gave *cyclohexane-1:1*-dicarboxylic acid (XLVIII) unaccompanied by any trace of 1-carboxy*cyclohexane-1*-acetic acid (LIII).



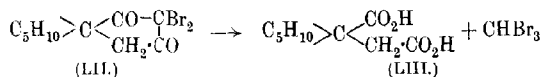
The aconitic acid derivative (XXI) was at once recognised as such by its close resemblance to the dimethyl analogue described by Farmer, Ingold, and Thorpe (*loc. cit.*). Thus it showed the same tendency to crystallise in combination with benzene, and an even greater tendency to pass into the corresponding anhydro-acid, the remarkable stability of which is easily interpreted on the basis of its spirane structure (XLIX). On heating with water, it passed into the corresponding itaconic acid (L), just as in the dimethyl series, at the same time yielding a very small amount of a saturated lactonic acid (LI). On oxidation with alkaline permanganate, it passed nearly quantitatively into *cyclohexane-1:1*-dicarboxylic and oxalic acids.



The only other substance the constitution of which has not been dealt with in the course of the preceding account is the resorcinol-like enol (XXXVI or XXXVII). That the hydroxyl groups in this substance are in the 1:3-positions despite the fact that it arises by hydrolysis of 2:3- or 3:4-disubstitution product follows because on bromination it yields the bromo-enol (XLI or XLII), and then a dibromo-diketone (LII) which is entirely non-enolic, and contains labile bromine, hypobromous acid and the monobromo-enol,



being produced by mere treatment with cold alkali. Treatment of any of these substances with excess of bromine and alkali results in oxidation to bromoform and carboxycyclohexaneacetic acid (LIII), the yield of the latter being quantitative :



The mono- and di-carboxylic acids (XVII, XVIII, and XIII, XV) both yield extremely stable ethyl esters, the former distilling in the neighbourhood of 300° under atmospheric pressure without any trace of decomposition, as is shown by the fact that the distillate, which immediately solidifies in the receiver, has the m. p. of the pure recrystallised material. An experiment in which a large quantity of the dicarboxylic ester was oxidised in aqueous-alcoholic solution with cold ferrieyanide in the presence of excess of alkali yielded the interesting result that along with a good yield of the semi-quinone (XIV) there was obtained a very small quantity of the analogue (XII) of caronic acid, the formation of which in the *gem*-dimethyl series constituted the principle item of evidence for the existence of the bridged bond.

EXPERIMENTAL.

(Note: Substances showing intra-annular tautomerism are designated by the names of their bridged modifications.)

Ethyl 5-cyclohexanespirodicyclo-Δ²-penten-3-ol-1:2:4-tricarboxylate (Ethyl 5-cyclohexanespirodicyclopentan-3-one-1:2:4-tricarboxylate) (VIII, IX) was prepared in the form of its sodium-derivative by the method described by Ingold and Thorpe (*loc. cit.*), and converted by acid hydrolysis into 5-cyclohexanespirodicyclopentan-3-one-1:2-dicarboxylic acid (XIII and XV), hereinafter termed "the dibasic acid," and 5-cyclohexanespirodicyclo-Δ²-penten-3-ol-1-carboxylic acid (5-cyclohexanespirodicyclopentan-3-one-1-carboxylic acid) (XIX and XX), hereinafter termed "the monobasic acid."

(A). Oxidation of the Di- and Mono-basic Acids with Potassium Ferrieyanide.

Oxidation of the Dibasic Acid: Formation of 5-cyclohexanespirodicyclo-Δ²-penten-3-ol-1:4-dione (XIV) (hereinafter called "the 1:4-diketone").—The dibasic acid (10 grams) was added to a solution prepared by dissolving 198 grams of potassium ferrieyanide and 48 grams of potassium carbonate in 840 c.c. of water.

The solution was kept for one hundred and twenty hours at 60° in a thermostat and then acidified with hydrochloric acid and extracted with ether. The residue obtained on drying and evaporating the ether at once solidified and was purified by crystallising first from water and then from a mixture of ether and ligroin (b. p. 40–60°) (Found: C = 66.46; H = 6.88. $C_{10}H_{12}O_3$ requires C = 66.63; H = 6.72 per cent.).

The substance forms silky needles, m. p. 134°. It is strongly enolic, giving a cherry red colour with ferric chloride, a greenish-blue copper salt, and titrating as a monobasic acid in the absence of carbonates (Found: $M = 178$. Calc., $M = 180$). It also forms an aniline derivative (below). It instantly decolorises cold alkaline permanganate, giving *cyclohexane-1:1-dicarboxylic acid*.

The *anilino-1:4-diketone*, $C_5H_{10}>C \begin{smallmatrix} \diagup CO \cdot CH \\ | \\ CO \cdot C \cdot NHPh \end{smallmatrix}$, was prepared by boiling the substance with aniline for about five minutes. The product was rubbed with dilute hydrochloric acid and crystallised from alcohol, from which it separated in orange needles, m. p. 150–151° (Found: C = 75.4; H = 6.9. $C_{16}H_{17}O_2N$ requires C = 75.3; H = 6.7 per cent.).

The *Bromo-1:4-diketone* (XXVI).—This substance, which was also encountered as an oxidation product of certain of the halogen derivatives of the mono- and di-basic acids, may be obtained by rubbing the diketone, m. p. 134°, with bromine and a little water, using 1.25 times the theoretical quantity of bromine. After half an hour, the excess of bromine is removed by the aid of the pump, and the pasty mass dried on porous porcelain, and crystallised successively from benzene and from a mixture of ether and light petroleum. It forms small, pale yellow needles, m. p. 190–191° (Found: Br = 30.7. $C_{10}H_{11}O_3Br$ requires Br = 30.9 per cent.). The substance gave a cherry-red colour with ferric chloride, and titration with barium hydroxide and phenolphthalein showed it to behave as a monobasic acid (Found: $M = 258$. Calc., $M = 259$).

The *Dibromo-triketone* (XLVII).—This substance was obtained by rubbing either the 1:4-diketone, m. p. 134, or its monobromo-derivative, m. p. 191, with excess of dry bromine. On removing the excess of bromine, a yellow, crystalline solid was obtained which could not be crystallised from water or organic solvents owing to the ease with which it lost bromine. It was therefore crystallised from bromine and was thus obtained as small, yellow nodules which decomposed above 100°. It gave no colour with ferric chloride and was not acidic, but cold dilute alkalis converted it into the monobromo-compound described above (Found: Br = 47.7. $C_{10}H_{10}O_3Br_2$ requires Br = 47.3 per cent.).

Oxidation of the Monobasic Acid : Formation of the 1:4-Diketone (XIV) and β :1-Dicarboxy- β :1-cyclohexanecarboxylic Acid (XXI).—This oxidation was carried out like the preceding one excepting that one hundred and eighty hours were allowed for the completion of the reaction. The product was isolated by extraction with ether, ground, and thoroughly extracted with cold benzene.

The 1:4-Diketone (XIV).—The benzene extract yielded this substance on evaporation. It was purified by crystallisation from water and identified with the previous specimen.

β :1-Dicarboxy- β :1-cyclohexanecarboxylic Anhydride (XLIX).—The solid insoluble in cold benzene was boiled with benzene and the filtered solution allowed to crystallise. The crystals contained loosely combined benzene which was lost at 100° or at the ordinary temperature in an evacuated desiccator. After drying at 100° , the substance became insoluble in benzene, and on analysis gave figures showing that it was the anhydro-acid (Found : C = 59.1; H = 5.5. $C_{11}H_{12}O_5$ requires C = 58.9; H = 5.3 per cent.). The portion insoluble in boiling benzene was the same substance.

The free tricarboxylic acid was obtained by boiling the anhydro-acid with water, but it could not be fully purified owing to its tendency to crystallise in combination with solvents and to the fact that solvent of crystallisation and water of constitution appeared to be lost more or less simultaneously. It is presumed, however, that the product obtained by treatment with water was the free tricarboxylic acid from the fact that it was completely soluble in benzene and gave approximately correct figures on titration with alkali.

Both the acid and anhydride are unsaturated, instantly decolorising cold alkaline permanganate. The principal products on oxidation in the usual manner with four atoms of available oxygen in the form of permanganate are cyclohexanedicarboxylic acid and oxalic acid.

cyclohexylidene succinic Acid (L).—This acid is the main product which is obtained when the above tricarboxylic acid or its anhydro-acid is heated with water in a sealed tube at about 200° for three hours. It is nearly insoluble in cold water and crystallises from the aqueous solution on cooling and scratching. It forms fine, hair-like needles, m. p. 175° (Found : C = 60.33; H = 7.27. $C_{10}H_{14}O_4$ requires C = 60.57; H = 7.12 per cent.). It instantly decolorises cold alkaline permanganate, and gives an odour of cyclohexane with the warm reagent.

Lactone of α -Hydroxy-1-carboxy- β :1-cyclohexanedicarboxylic Acid (LI).—The mother-liquors from the unsaturated acid were evaporated to dryness and the residue was crystallised from a mixture of

ether and ligroin. It melted at 206° (Found: C = 54.73; H = 5.76. $C_{10}H_{14}O_6$ requires C = 54.54; H = 5.83 per cent.), and titration in the cold showed it to be a dibasic acid (Found: $M = 242$. Calc., $M = 242$).

(B). *Oxidation of the Di- and Mono-basic Acids by Alkaline Permanganate.*

Oxidation of the Dibasic Acid. Formation of α -Ketocyclohexane-1:1-diacetic Acid (XVI) and Oxalic Acid.—The dibasic acid (3 grams) together with potassium carbonate (2 grams) was dissolved in water and titrated in the cold with a 3 per cent. solution of potassium permanganate. Four atoms of available oxygen were absorbed, the last 0.5 atom rather slowly. The oxides of manganese were collected and extracted with water and steam, and the combined aqueous filtrates concentrated, acidified with hydrochloric acid, rendered just alkaline with ammonia, and treated with calcium chloride. The calcium oxalate was collected and identified in the usual way, and the filtrate acidified with hydrochloric acid and extracted with ether. The residue from the ether was crystallised from chloroform and thus obtained as small prisms, m. p. 131° (Found: C = 55.8; H = 6.53; M by titration = 214. $C_{10}H_{14}O_5$, dibasic, requires C = 56.0; H = 6.57 per cent.; $M = 214$).

The quinoxaline (XLIII) was prepared by dissolving equivalent quantities of the ketonic acid and *o*-phenylenediamine in a little alcohol, evaporating to a somewhat smaller bulk, and then cooling, when it separated in orange-red needles, m. p. 246° (decomp.) (Found: N = 9.68. $C_{16}H_{18}O_2N_2$ requires N = 9.86 per cent.).

Reduction to α -Hydroxycyclohexane-1:1-diacetic Acid (XLIV).—The ketonic acid was reduced in aqueous solution with a large excess of 4 per cent. sodium amalgam, carbon dioxide being passed through the liquid throughout the process. The liquid was acidified and exhaustively extracted with ether. The product rapidly solidified on seeding with a crystal (Beesley, Ingold, and Thorpe, *loc. cit.*) of the lactone of the above hydroxy-acid, and was then crystallised from a mixture of benzene and light petroleum and identified by the method of mixed melting point.

Oxidation of the Monobasic Acid. Formation of α -Ketocyclohexane-1:1-diacetic Acid (XVI).—This oxidation was carried out like the preceding one excepting that five atoms of available oxygen were employed. Oxalic acid was not obtained, and the acid extracted with ether contained gummy impurities, which were removed by converting into the calcium salt, washing this with alcohol and ether, and then regenerating the acid. It was identified

by direct comparison with the substance obtained from the dibasic acid (above).

(C). *Halogen Derivatives of the Di- and Mono-basic Acids.*

4-Bromo-5-cyclohexanespirodicyclo- Δ^2 -penten-3-ol-1:2-dicarboxylic Acid (4-Bromo-5-cyclohexanespirodicyclopentan-3-one-1:2-dicarboxylic Acid) (XXII and XXIII) (hereinafter called "the monobromo-dibasic acid").—The dibasic acid (2 grams) was dissolved by warming in acetic acid, and the solution treated at 40–50° with 1.2 times the theoretical quantity of a 10 per cent. solution of bromine in acetic acid. The solution became colourless after a short time and was then allowed to evaporate at the ordinary temperature. The crystalline residue was purified by crystallisation from a mixture of ether and benzene, from which it separated in small prisms, m. p. 197–198° (Found: Br = 25.3. $C_{12}H_{13}O_5Br$ requires Br = 25.2 per cent.). It gives a deep red colour with ferric chloride.

2:4-Dibromo-5-cyclohexanespirodicyclopentan-3-one-1:2-dicarboxylic Acid (XXIV) (hereinafter called "the dibromo-dibasic acid").—The dibasic acid (2 grams), dissolved in 30 c.c. of glacial acetic acid, was treated with 1.5 times the theoretical amount of a 10 per cent. solution of bromine in acetic acid, and then saturated with dry hydrogen bromide. After keeping for forty-eight hours at the ordinary temperature, the solution was evaporated at the ordinary temperature and the crystalline residue purified by crystallisation from chloroform or a mixture of ether and benzene. The acid, m. p. 217–218° (Found: Br = 40.1. $C_{12}H_{12}O_5Br_2$ requires Br = 40.4 per cent.), gives no colour with ferric chloride, which converts it into an insoluble iron salt.

4-Bromo-5-cyclohexanespirodicyclo- Δ^2 -penten-3-ol-1-carboxylic Acid (4-Bromo-5-cyclohexanespirodicyclopentan-3-one-1-carboxylic Acid) (XXVII and XXVIII) (hereinafter called "the monobromo-monobasic acid").—This substance was prepared from the monobasic acid just as the monobromo-dibasic acid was from the dibasic acid. The crystalline product was purified by crystallisation first from a mixture of ether and ligroin and then from ether. It forms needles, m. p. 197–198° (Found: C = 48.5; H = 5.1. $C_{11}H_{13}O_5Br$ requires C = 48.0; H = 4.8 per cent.).

2:4-Dibromo-5-cyclohexanespirodicyclo- Δ^2 -penten-3-ol-1-carboxylic Acid (2:4-Dibromo-5-cyclohexanespirodicyclopentan-3-one-1-carboxylic Acid) (XXIX and XXX) (hereinafter called "the dibromo-monobasic acid").—The monobasic acid (2 grams) was dissolved in chloroform and treated with 1.2 times the theoretical amount of a 5 per cent. solution of bromine in chloroform. While

the first half of the bromine solution was being added the solution was shaken vigorously until decoloration took place. The second half was added in one lot and the solution kept in the dark for sixteen hours, after which the solvent was evaporated at the ordinary temperature, and the product crystallised from a mixture of ether and ligroin. The separation of admixed mono- and tribromo-derivatives is a matter of some difficulty, but having fortuitously obtained a pure specimen (m. p. 152–153°) of the dibromo-acid it is usually possible to seed it out from solution in moderately good yield (Found: C = 37.8; H = 3.53. $C_{11}H_{12}O_3Br_2$ requires C = 37.5; H = 3.44 per cent.).

2 : 2 : 4-*Tribromo-5-cyclohexanespirodicyclopentan-3-one-1-carboxylic Acid* (XXXII) (hereinafter called "the tribromo-monobasic acid").—This substance was prepared from the monobasic acid just as the dibromo-dibasic acid was from the dibasic acid, excepting that the quantity of bromine used was 1.25 times the theoretical. The product was crystallised from a mixture of ether and ligroin, from which it separated in minute prisms, m. p. 163–165° (Found: Br = 55.64. $C_{11}H_{11}O_3Br_3$ requires Br = 55.86 per cent.).

(D) *Oxidation of the Five Bromo-acids by Ferricyanide.*

Oxidation of the Monobromo-dibasic Acid: Formation of the 1 : 4-Diketone (XIV) and Dicarboxycyclohexanecarboxylic Acid (XXI).—A solution of the monobromo-dibasic acid (1.25 grams), potassium ferricyanide (25 grams), and potassium carbonate (8 grams) in 100 c.c. of water was kept at 60° for forty-eight hours, cooled, acidified with hydrochloric acid, and extracted with ether. The product was separated and identified exactly as described on p. 866.

Oxidation of the Dibromo-dibasic Acid: Formation of the Bromo-1 : 4-diketone (XXVI).—A solution of the dibromo-dibasic acid (1.5 grams), potassium ferricyanide (25 grams), and potassium carbonate (8 grams) in 100 c.c. of water was kept at 60° for one hundred and twenty hours and the acid product isolated in the usual way. After one crystallisation from benzene, it melted at 190–191°, and did not depress the m. p. of the previous specimen of bromo-diketone (*M* by titration = 259. Calc., *M* = 258). The yield was nearly quantitative.

Oxidation of the Monobromo-monobasic Acid: Formation of the 1 : 4-Diketone (XIV) and Dicarboxycyclohexanecarboxylic Acid (XXI).—A solution of the monobromo-monobasic acid (1.25 grams), potassium ferricyanide (25 grams), and potassium carbonate (8 grams) in 100 c.c. of water was kept at 60° for eight hours and the products of oxidation were isolated, separated, and identified as described on p. 866.

Oxidation of the Dibromo-monobasic Acid: Formation of the Bromo-1:4-diketone (XXVI) and Bromodicarboxycyclohexanecarboxylic Acid (XXXI).—The dibromo-monobasic acid (1.5 grams), potassium ferrieyanide (25 grams), and potassium carbonate (8 grams), dissolved in 100 c.c. of water, were heated at 60° for six hours and the products of oxidation isolated as usual by extraction with ether and then dried at 100°. On extraction by boiling benzene, a considerable quantity of the bromo-1:4-diketone crystallised from the solution on cooling (Found: Br = 30.8 per cent.; $M = 258$ by titration; m. p. 191°), whilst an insoluble residue consisting of α -bromo- β :1-dicarboxy- β -cyclohexanecarboxylic anhydro-acid remained. This substance separated from ether as microscopic prisms, m. p. 155–158° (decomp.) (Found: Br = 26.4. $C_{11}H_{11}O_5Br$ requires Br = 26.4 per cent.), and at once decolorised cold alkaline permanganate. It was not found possible to isolate the free tricarboxylic acid.

Oxidation of the Tribromo-monobasic Acid: Formation of the Bromo-1:4-diketone (XXVI).—The tribromo-monobasic acid (1.5 grams), potassium ferrieyanide (25 grams), and potassium carbonate (8 grams), dissolved in 100 c.c. of water, were heated for eight hours at 60° and the product was isolated as usual by extraction with ether. Crystallised from benzene, it melted at 190–191° and was identified as the bromo-diketone. The yield was nearly quantitative.

(E). *Action of Boiling Alkali on the Five Bromo-acids.*

Hydrolysis of the Monobromo-monobasic Acid: Formation of 1:3-Dihydroxy-5-cyclohexanespiro[1-cyclo-2-pentene] (XXXVI and XXXVII) (hereinafter called "the 1:3-dihydroxy-compound").—The monobromo-monobasic acid was boiled with 5 per cent. aqueous potassium hydroxide (4 mols.) for two hours. The liquid was cooled, extracted with ether, acidified with hydrochloric acid, and again extracted. The residue from the second extract quickly solidified and was crystallised first from ether and then from chloroform, from which it separated in prisms, m. p. 179–180° (Found: C = 72.6; H = 8.8. $C_{10}H_{11}O_2$ requires C = 72.3; H = 8.5 per cent.).

The 1:3-dihydroxy-compound is strongly enolic, giving a marked red colour with ferric chloride and a blue copper salt. It liberates carbon dioxide from alkaline hydrogen carbonates and on titration in aqueous solution with carbonate-free alkaline hydroxide it gives figures which indicate an appreciable acidity for the second enol residue, and on titration with sodium ethoxide in alcohol fairly accurate dibasicity values are obtained. It does not react with

hydroxylamine, phenylhydrazine, or semicarbazide in acetic acid solution, but in "coupling" reactions it behaves in alkaline solution in the normal manner of a "second component," giving brick-red azo-dyes with diazotised aniline, sulphanilic acid, etc.

*Oxidation to 1-Carboxycyclohexane-1-acetic Acid (LIII).—*The 1:3-dihydroxy-compound (1.0 gram), dissolved in a small excess of sodium hydroxide, was treated at 0° with bromine (1 c.c.), dissolved in just sufficient sodium hydroxide to give a colourless solution. A cloud of bromoform soon appeared, and the solution was then warmed until clear, cooled, acidified with hydrochloric acid, and extracted with ether. The residue from the extract was crystallised from water, from which it separated in stout needles, m. p. 132–133° (Found: C = 58.0; H = 7.5. Calc., C = 58.0; H = 7.5 per cent.). It was identified by comparison with a specimen recently prepared by a different method by Mr. Dickens of this laboratory.

*Bromination to the 2-Bromo-1:3-dihydroxy-compound (XLI and XLII).—*The 1:3-dihydroxy-compound (1.5 grams) was dissolved in chloroform and treated with a chloroform solution containing 2.2 atoms of bromine. After keeping over-night, the liquid was evaporated and the product crystallised from ethyl acetate. It gives an intense blood-red coloration with ferric chloride and on titration with alkali behaves like the 1:3-dihydroxy-compound. It melts with decomposition at 244° (Found: Br = 32.7. $C_{10}H_{13}O_2Br$ requires Br = 32.6 per cent.).

*Hydrolysis of the Dibromo-monobasic Acid: Formation of the 4-Bromo-1:3-dihydroxy-compound (XXXVIII and XXXIX).—*The dibromo-monobasic acid (1.5 grams) and potassium hydroxide (1.0 gram) were dissolved in 20 c.c. of water and boiled for one and three-quarter hours. The product was extracted with ether, acidified with hydrochloric acid, and again extracted with ether. The neutral extract contained a small quantity of a volatile substance with a camphor-like odour, but there was not sufficient for purification. The acid extract yielded a solid residue, which after crystallisation from a mixture of ether and ligroin melted at 228–229°. This melting point was depressed by the addition of a small amount of the isomeric bromo-dihydroxy-compound (m. p. 244°) mentioned above, and the two compounds differed in other respects, for example, in the intensity of the colour with ferric chloride, the more fusible isomeride giving a colour of only moderate depth (Found: Br = 32.7. $C_{10}H_{13}O_2Br$ requires Br = 32.6 per cent.).

*Hydrolysis of the Tribromo-monobasic Acid: Formation of the 2-Bromo-1:3-dihydroxy-compound (XLI and XLII).—*The tribromo-

monobasic acid was boiled for two hours with a 10 per cent. excess of 5 per cent. aqueous sodium hydroxide. The acid product was isolated as in the preceding example and crystallised from ethyl acetate. It was identified by direct comparison with a specimen of the same substance prepared by direct bromination, and by oxidation.

*Oxidation to 1-Carboxycyclohexane-1-acetic Acid (LIII).—*This oxidation was carried out like that described on p. 871, 1·5 grams of the bromo-dihydroxy-compound being used for 1 c.c. of bromine. The acid was identified by titration ($M = 186$. Calc., $M = 186$) and by direct comparison and a mixed melting point determination with an authentic specimen.

*Hydrolysis of the Monobromo-dibasic Acid: Formation of the 1:3-Diketone (XXXVI and XXXVII).—*The hydrolysis of the monobromo-dibasic acid was carried out exactly like that of the monobromo-monobasic acid, and the product was isolated, purified, and identified in the same way.

Hydrolysis of the Dibromo-dibasic Acid: Formation of the 2-Bromo- and 4-Bromo-derivatives of the 1:3-Dihydroxy-compound.—This hydrolysis was conducted like that of the tribromo-monobasic acid and the product isolated in the same way. The product, on rubbing with cold ethyl acetate, yielded the 2-bromo-1:3-dihydroxy-compound, which was finally purified by crystallisation from the same solvent. The ethyl acetate extract on evaporation gave a semi-solid residue, which was drained for several days on porous porcelain, and then extracted with a warm mixture of equal volumes of ether and light petroleum. The solution, on cooling, deposited the 4-bromo-1:3-dihydroxy-compound. The two isomerides were identified by direct comparison and by determination of mixed melting points with genuine specimens.

(F). *The Esters of the Mono- and Di-basic Acids.*

Ethyl Ester of the Monobasic Acid.—The acid (5 grams) was heated with 20 c.c. of ethyl alcohol and 7 c.c. of concentrated sulphuric acid until a clear solution was obtained. Heating was then continued on the steam-bath for eight hours, and the product poured into water, and separated by ether and sodium carbonate into neutral and acid fractions. The acid fraction gave 0·5 gram of unchanged acid, whilst the neutral fraction yielded a crystalline residue, which in the crude state melted at 63–65°. After crystallisation from light petroleum, it melted at 64·5–65° and the m. p. was not altered by further crystallisation. The easiest way to purify the ester, however, is to distil it at ordinary pressure, when it boils at 29·5° without decomposition, and solidifies in the receiver

to a colourless, crystalline mass, m. p. $64.5-65^{\circ}$ (Found: C = 70.35; H = 8.1. $C_{13}H_{18}O_3$ requires C = 70.3; H = 8.1 per cent.). Boiling with hydrochloric acid hydrolyses it to the original acid.

The *semicarbazone*, prepared in aqueous-alcoholic solution from the ester and semicarbazide acetate, separated from alcohol in needles, m. p. $183-185^{\circ}$ (Found: C = 60.0; H = 7.6. $C_{14}H_{21}O_3N_3$ requires C = 60.2; H = 7.5 per cent.).

Diethyl Ester of the Dibasic Acid.—A mixture of 5 grams of the acid, 20 c.c. of ethyl alcohol, and 7 c.c. of concentrated sulphuric acid was heated on the steam-bath for eight hours. The ester was isolated in the usual way and purified by distillation. It is a colourless oil, b. p. $236-238^{\circ}/20$ mm., and gives a red colour with ferric chloride. It is soluble in concentrated aqueous potassium hydroxide, giving a yellow solution, from which the original dibasic acid can be recovered after acidification (Found: C = 65.1; H = 7.6. $C_{16}H_{22}O_5$ requires C = 65.3; H = 7.5 per cent.).

The *semicarbazone*, prepared like that mentioned above, separated from alcohol in colourless needles, m. p. $121-123^{\circ}$ (Found: C = 58.0; H = 7.0. $C_{17}H_{25}O_5N_3$ requires C = 58.1; H = 7.1 per cent.).

Oxidation of the Monoethyl Ester by Permanganate.—The ester (5 grams), dissolved in acetone, was treated with a solution of potassium carbonate (3 grams) in water and one of potassium permanganate (9 grams) in the minimal quantity of 75 per cent. acetone. The mixture was kept for twenty-four hours, evaporated, and filtered. The oxides of manganese were treated with steam, and the combined aqueous filtrates were acidified, concentrated, and extracted with ether. The residue from the extract was boiled with hydrochloric acid, and the product extracted with ether and crystallised from chloroform. It was identified as α -ketocyclohexane-1:1-diacetic acid by direct comparison with an authentic specimen, and by the formation of the quinoxaline previously mentioned.

Oxidation of the Diethyl Ester by Permanganate.—This experiment was carried out like the last, and the product (α -ketocyclohexane-1:1-diacetic acid) isolated and identified in the same way.

Oxidation of the Monoethyl Ester by Ferricyanide.—The ester (3 grams) was dissolved in 50 per cent. ethyl alcohol and treated with successive tenths of a solution prepared by dissolving 50 grams of potassium ferricyanide and 100 grams of potassium hydroxide in 500 c.c. of water. The ten lots were added with an equal volume of alcohol every twelve hours, the solution being kept at 0° . It was then kept at the ordinary temperature for two days, and there-

after acidified and extracted with ether. The residue from the ether was hydrolysed with hydrochloric acid, and the products of hydrolysis were separated and identified as the 1:4-diketone and dicarboxy*cyclohexane*acrylic anhydro-acid in the manner described on p. 866.

Oxidation of the Diethyl Ester with Ferricyanide.—This experiment was carried out like the preceding one and the products of oxidation were isolated and hydrolysed in the same way. The products of hydrolysis consisted almost solely of the 1:4-diketone, but on extracting this with successive small quantities of a mixture of benzene and ligroin a small residue was obtained which gave scarcely any colour with ferric chloride and melted at about 150–175°. After crystallisation from water, it melted with decomposition at 196–198°, and gave no trace of colour with ferric chloride, and although the quantity was too small for analysis there is scarcely room for doubt that it was the *cis*-form of *cyclohexane-spirocyclopropanedicarboxylic acid* (XII), because it did not lower the m. p. of a genuine specimen of that substance and also gave almost correct value on titration (Found: $M = 201$. Calc. $M = 198$).

We wish to thank the Royal Society for a grant which has largely defrayed the cost of this investigation.

IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,

SOUTH KENSINGTON, S.W. 7. (*Received, February 2nd, 1921.*)

CIV.—*Studies in Organic Compounds containing Sulphur. Part I. The Effect on General Absorption due to the Valency and Mode of Linkage of the Sulphur Atom.*

By DAVID TEMPLETON GIBSON, HUGH GRAHAM, and JAMES REID.

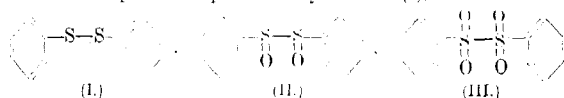
SEVERAL series of open-chain and ring compounds containing sulphur have been examined spectrographically. In this paper, the valency and linkage effects are considered in relation to absorption spectra, whilst in a further communication it is proposed to deal with the effect of tautomeric change on the absorption of organic sulphur compounds.

The following compounds, in which sulphur is present in the molecule as a member of an open chain, were examined; diphenyl sulphide, diphenyl disulphide, dibenzyl sulphide, and their sulphoxides and sulphones; benzenesulphinic acid and its sodium

salt; and phenyl methyl sulphone. The ring compounds studied were 1:4-dithian (diethylene disulphide), diethylene disulphoxide, 1:4-thioxan, thianthren, and thianthren monosulphoxide. The substances were prepared by the known methods. For a sample of thianthren monosulphoxide we are indebted to Professor Smiles. The substances were all carefully purified before use. Alcoholic solutions were used for spectrographic examination. The iron arc was the source of radiation.

The effect on general absorption of compounds, in the molecule of which sulphur forms part of a chain, will be considered first. We must therefore select a part of the spectrum removed from the banded region to avoid the interference of factors which have an influence on selective absorption. On examination of the absorption curves of the series diphenyl disulphide, diphenyl disulphoxide and diphenyl disulphone, it is seen that the absorptive power of diphenyl disulphide is much greater than that of the disulphoxide, and the disulphoxide is markedly more absorptive than the disulphone (Fig. 1), the limits of absorption being 2850, 3150, and 3400 oscillation frequencies at logarithm of relative thickness 4.0 of $M/100,000$ -solution for the disulphide, the disulphoxide, and disulphone, respectively.

If the disulphide is represented by formula (I),



the presence of residual valency being indicated by means of the dotted lines, it will be seen that the centre of residual valency represented by the two sulphur atoms is conjugated with the benzenoid centres of unsaturation. If the disulphoxide be represented in a similar manner (II), examination of the formula will show that there is present in the molecule what Thiele called a system of "crossed double bonds."

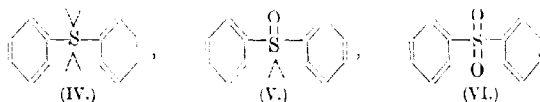
An exhaustive study of the influence of conjugated unsaturated groupings of the types $>C=C<$, $>C=O$, and $>C=N-$ on general absorption has been made by Crymble, Stewart, Wright, and Glendinning (T., 1911, **99**, 451), Crymble, Stewart, Wright, and Rea (*ibid.*, 1260), and Macbeth, Stewart, and Wright (T., 1912, **101**, 599), who have shown that a substance containing a single straight system of conjugated bonds in the molecule has an absorptive power greater than that of one containing a system of "crossed double bonds."

Reverting to diphenyl disulphoxide, the union of two oxygen atoms with the two sulphur atoms creates two new centres of

unsaturation, whilst the unsaturation between the sulphur atoms is not completely destroyed. These new centres are also conjugated with the centres of unsaturation in the benzene nuclei. Thus the introduction of "cross conjugation" into the molecule leads to decrease of general absorption.

Consider now the case of the further oxidation product, namely, the disulphone (formula III). In this molecule the effective change from the disulphoxide is the replacement of a centre of unsaturation between two sulphur atoms by a side chain sulphur-oxygen centre of unsaturation. In other words, there is an increase of "crossed unsaturation" conjugated with the benzene nuclei. One would therefore expect this substance to show weaker general absorption than either the disulphide or the disulphoxide. Inspection of the curves (Fig. 1) shows that this expectation is realised.

Extending these ideas to diphenyl sulphide and its oxygen derivatives, if we regard the sulphur atom of diphenyl sulphide as a centre of residual affinity, we have in this case also a straight chain of conjugated centres of unsaturation (formula IV), and in the sulfoxide (V) and sulphone (VI) molecules "crossed" systems of conjugation. The relative general absorptive powers of the three compounds of this series are in the same order as in the disulphide series, that is, the sulphide shows greater general absorption than the sulfoxide, and the sulfoxide is more absorptive than the sulphone.

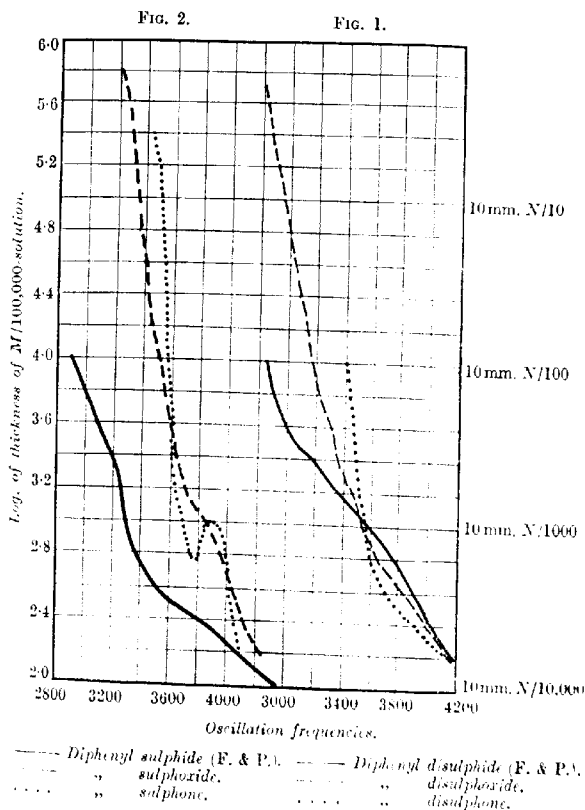


To put these ideas to a further test we have examined dibenzyl sulphide, the sulfoxide, and the sulphone. In these molecules the sulphur centre of unsaturation is isolated from the benzene centres by the interposition of saturated methylene groups. There is no conjugation in these cases, and examination of the absorption curves (Fig. 3) shows that the differences in general absorption are not so marked as in the cases already examined, and the order of relative absorptive power no longer holds. With the elimination of the predominating influence of conjugation the effects due to other influences are apparent.

Turning to the compounds in which sulphur is present in the molecule as a ring member, comparison of the absorption curves of 1:4-dithian and its disulphoxide (Fig. 4) shows that the latter is the more absorptive, the limits of absorption in oscillation frequencies being 3440 and 3760 for the disulphoxide and disulphide,

respectively, at 5.8 log. of relative thickness of $M/100,000$ -solution.

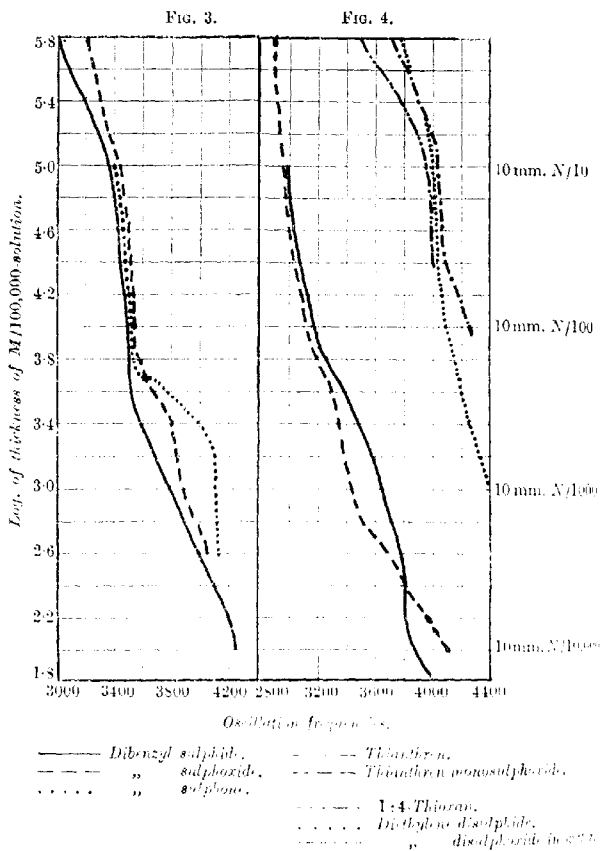
On examination of the curve of thianthren and thianthren monosulphoxide (Fig. 4), in which sulphur atoms also occupy positions in a ring system, it is found that the same relationship holds.



The absorptive power of the sulfoxide is greater than that of thianthren, the limits of absorption being 3000 and 3100 oscillation frequencies at 4.6 log. of relative thickness of $M/100,000$ -solution.

The absorption of these ring compounds is anomalous when compared with that of the open-chain substances, and on this account we have extended our study to 1:4-thioxan. The structure of

1:4-thioxan is the same as that of 1:4-dithian except that a sulphur atom has been replaced by an oxygen atom. Comparison of the curves (Fig. 4) of these two compounds shows that 1:4-thioxan is the more absorptive at the higher concentrations.

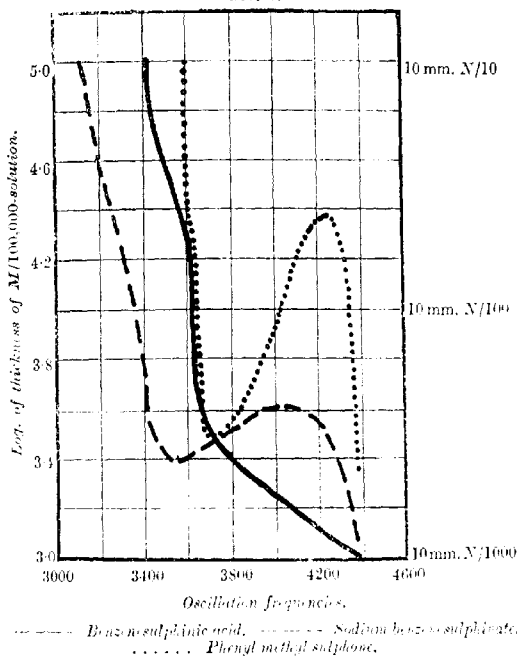


Purvis, Jones, and Tasker (T., 1910, 97, 2287), from an examination of several series of thio-compounds, have shown that the replacement of oxygen by sulphur causes a marked increase in the absorptive power of a compound. The ring compounds 1:4-dithian and 1:4-thioxan, therefore, are also anomalous cases.

On account of these variations from the general rules as judged by comparison with open-chain compounds, it is of interest to consider here some of the other properties of these ring compounds and their derivatives.

Masson (T., 1886, 49, 233) and Mansfeld (*Ber.*, 1886, 19, 700) found that 1:4-dithian behaves abnormally in certain respects. For example, in the presence of a large excess of boiling methyl

FIG. 5.



iodide it yields the mono-additive compound only and not the di-compound as would be expected.

Clarke and Smiles (T., 1909, 95, 994) have studied the properties of diethoxythioxan. They find that this sulphide has not the properties of a substance in which bivalent sulphur is united to saturated hydrocarbon groups; it does not combine with mercuric halides, and the addition of alkyl iodide proceeds extremely slowly.

The anomalous character of 1:4-thioxan and 1:4-dithian was further shown by Clarke (T., 1912, 101, 1788), who found that the

replacement of one of the sulphur atoms of 1:4-dithian by oxygen causes a great decrease in the reactive power of the sulphur atom remaining as measured by the velocity of combination with bromo-acetophenone.

It is clear from the evidence given that in these compounds chemical reactivity and absorption spectra are closely associated. We are at present preparing other cyclic compounds containing sulphur in the ring and allied compounds for fuller spectrographic examination, and hope to throw some light on this interesting question of residual affinity and the mutual influence of unsaturated atoms on one another.

Let us now consider some other aspects of the subject.

When the absorption curves of a series of compounds such as diphenyl sulphide, its sulfoxide and sulphone are compared (Fig. 2) in the banded region, it is interesting to note the effect on selective absorption due to the different stages of unsaturation of the sulphur atom.

The curves of this series show, with increasing saturation of the sulphur atom, gradual development of effects due to the benzene nuclei: thus comparing the curves of the sulphide and sulphone (Fig. 2), it is seen that the sulphide shows general absorption only, whereas the sulphone exhibits a band of small persistence in the region 3800-4000 oscillation frequencies which is the region of the characteristic benzene bands. Examination of the curves of diphenyl disulphide and its sulphone shows that the trend of the change in absorption is of a similar nature, although no band is developed in the case of this sulphone, only rapid extension being apparent in the benzene band region.

It seems probable that the alteration of the vibrations in the benzene nucleus, which give rise to selective absorption, is due in part to the residual affinity of the sulphur atom in the molecule. Fox and Pope (T., 1913, 103, 1263) have arrived at a similar conclusion from a comparative study of corresponding oxygen and sulphur derivatives of benzene such as phenol and thiophenol.

We have further studied the absorption spectra of the series of compounds benzenesulphinic acid, sodium benzenesulphinate, phenyl methyl sulphone.

The absorption curves of these substances are of interest in view of their bearing on the constitution of benzenesulphinic acid. Smiles and Le Rossignol (T., 1906, 89, 696) state that this acid reacts in acid solution according to formula (VII), whilst the sodium salt behaves as (VIII).



The evidence of the absorption curves of these compounds is in accordance with this view. Benzenesulphinic acid, which contains an unsaturated sulphur atom in the molecule, shows general absorption (Fig. 5); on the other hand, benzenesulphonic acid (Wright, T., 1914, 105, 673) and phenyl methyl sulphone, whose molecules contain fully saturated sulphur, show selective absorption (Fig. 5). Sodium benzenesulphiniate also shows a shallow band.

Conclusions.

- (1) A substance containing in the molecule unsaturated sulphur in "straight chain conjugation" with benzene centres of unsaturation shows greater general absorption than a similar substance into the molecule of which "crossed conjugation" has been introduced.
- (2) Certain compounds in which sulphur is present in the molecule as a member of a ring system show anomalous general absorption compared with open-chain compounds.
- (3) The residual affinity of a sulphur atom in a molecule is accountable, in part, for the alterations of those vibrations of the benzene nucleus which give rise to selective absorption.

We wish to express our thanks to Professors Stewart and Smiles for the interest they have shown in this work, and to the Research Fund Committee of the Chemical Society for a grant.

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[Received, March 6th, 1923.]

CV.—Isolation of the Oxide of a New Element. A Correction.

By ALEXANDER SCOTT.

IN the short paper (this vol., p. 312) in which I described what seemed to be the oxide of a new element I mentioned that I had offered to send my preparations to Drs. Coster and Hevesy for examination by them by means of X-ray spectral analysis and for comparison with their own. They replied very kindly that they would gladly do so and accordingly I sent to Copenhagen all that remained of the pale buff-coloured powder labelled "New Oxide" and all the cinnamon-coloured oxide recovered from the atomic weight determination by means of the fluoride (in each case between 0.3 and 0.4 of a gram) together with some of the original New Zealand sand.

The result of their first examination, which I communicated to the Society at its meeting on February 15th, was to the effect that

they had been unable to detect any of the hafnium lines in any of my specimens.

They have since subjected my specimens, and especially the oxide from the fluoride, to a most searching and prolonged examination both by means of X-ray and by optical spectral analysis in the hope of finding in them some of the other missing elements, and in particular that of atomic number 75, but without success. They conclude as the result of their examination that the chief constituents are oxides of iron and titanium along with traces of other elements, all previously known.

I received their final report on March 19th, having received the preparations a few days previously, and at once set to work to unravel the mystery.

The cinnamon-coloured oxide which remained weighed 0.1763 gram and was fused with sodium bisulphate, in which it went entirely and easily into solution. The melt was dissolved in water and boiled, when there separated out 0.1591 gram apparently of titanium dioxide having a faint lemon tint, and from the filtrate 0.0097 gram of oxides was precipitated by ammonia, thus accounting for 0.1688 gram of the quantity taken. The precipitate produced by ammonia had only a faint brown tint and looked like alumina containing a minute quantity of iron. The whole was once more brought into solution by means of fusion with sodium bisulphate and the iron (estimated colorimetrically) amounted to 0.0011 gram of ferric oxide.

In order to prepare the specimen used for the atomic weight determinations (this vol., pp. 311 and 312), 1 gram of the "New Oxide" was taken and to it was added pure potassium carbonate in slight excess above the amount which would be required for the formation of the double fluoride, on the assumption that the atomic weight of the new element was 175. Excess of hydrofluoric acid was added, when all went into solution on the water-bath. The solution was allowed to cool and settle in a deep platinum crucible, when a fairly large quantity of potassium silicofluoride separated out. The transparent nature of this precipitate and its almost invisibility in a platinum vessel led to its amount being under-estimated at the time. Its importance, however, became apparent when the cause of the high atomic weight value came to be sought for. Its weight was 0.7225 gram.

The solution separated from the potassium silicofluoride was now evaporated down and, on cooling, characteristic scaly crystals separated out which, after pouring off the mother-liquor, were washed with cold water and dried at 100°. The weight of this fraction was 0.615 gram.

The mother-liquors when concentrated again gave the sealy crystals on cooling and the addition of a small quantity of alcohol produced a further separation of crystals which under the microscope seemed to be exactly similar in form to those from the aqueous solution. The whole was therefore evaporated to dryness and was found to weigh 0.780 gram.

This last fraction was deliberately chosen for the first determination of the atomic weight, as it was anticipated that the results would undoubtedly err on the side of being too low rather than too high because of the presence of fluorides which were assumed to be those of potassium and sodium.

The results are those already given (this vol., p. 312) in which 0.7752 gram of salt gave 0.4057 gram of oxide.

It was not until the purer fraction of crystals was similarly treated in order to get a more accurate atomic weight for the element that any doubt suggested itself as to the nature of the oxide. Two determinations were made by the same method, namely, treatment of the salt with strong sulphuric acid, the excess of acid driven off, followed by prolonged ignition alone and finally along with ammonium carbonate to decompose the sulphates of the titanium group. The oxide was then washed free from potassium sulphate and weighed.

In the first experiment 0.2216 of salt gave 0.0820 of oxide and
in the second " 0.3724 " " " 0.1361 " "

0.5940 of salt gave 0.2181 of oxide.

This equals 36.7 per cent.

K_2TiF_6 would give 33.3 per cent. of TiO_2 .

K_2ZrF_6 " " 43.3 " " ZrO_2 .

In the first experiment, on the addition of ammonia to the potassium sulphate solution a small quantity of a brown precipitate came down which was identified as ferric hydroxide. In the second, the ferric hydroxide was collected and weighed as ferric oxide. Its weight was 0.0043 gram. If the proportionate amount be added for the first experiment, this would make the ferric oxide in the 0.594 gram of salt 0.0069 gram.

The potassium silicofluoride when similarly treated with sulphuric acid gave only 0.0051 gram of TiO_2 precipitated by boiling and 0.0053 gram on the addition of ammonia, that is 0.0104 gram in all.

The large amount of potassium silicofluoride, which was not dried and weighed until some days after the first atomic weight determinations were made, gave the clue to the mystery of the high atomic weight obtained.

It had been assumed that no silicate could have withstood the fusions to which the "New Oxide" had been subjected and that the pale buff-coloured powder remaining was an oxide or mixture of oxides. The formation of the insoluble potassium silicofluoride removed so much potassium from the solution that the final fraction used for the atomic weight consisted of double fluoride mixed with fluorides, not of potassium and sodium, but of iron and titanium, and these latter yielded no potassium sulphate, but only the insoluble oxides. This therefore gave the unduly high atomic weight, which seemed to be all that was required to prove that the "New Oxide" was that of the element of atomic number 72.

The amount of SiO_2 corresponding to 0.7225 gram of K_2SiF_6 is 0.197 gram. This is too high, as there was, as usual, a small quantity of hydrofluosilicic acid in the hydrofluoric acid employed. An experiment with a small quantity of "New Oxide" and pure potassium fluoride showed that it contained at least 0.164 gram of SiO_2 per gram.

Of the one gram of "New Oxide" taken, 0.8051 gram has been accounted for; 0.6289 gram of oxides precipitated from their solutions by boiling + 0.0122 precipitated by ammonia + 0.164 gram of SiO_2 . To check this, 0.0997 gram of "New Oxide" was extracted with hydrochloric acid, which left behind 0.0806 gram insoluble, dissolving only 0.0018 gram of titanium dioxide, a result which corresponds as closely as can be expected with the above amount from 1 gram. The difference is completely accounted for by the hygroscopic moisture and the soda pertinaciously retained by the powder. It ought to be mentioned that the "New Oxide" was what remained after its last fusion with sodium hydroxide and had been washed only with boiling water.

The very refractory substance in the New Zealand sand may therefore be regarded as titanium dioxide in which part of the titanium is replaced by silicon. Insoluble and refractory substances similar to that obtained by me have been found by other workers with titanium minerals. When I have obtained a larger supply of New Zealand sand from the same source I hope to be able to make a more complete analysis and examination of this substance than is possible with the small amount I now possess.

I cannot conclude without cordially thanking Professor Bohr, in whose laboratory the examination by Drs. Coster and Hevesy was carried out, and expressing to them my sincere appreciation of all their courtesy and the trouble they have taken in this matter.

34, UPPER HAMILTON TERRACE,
LONDON.

[*Received, April 3rd, 1923.*]

CVL.—*The Form of the Vapour Pressure Curve at High Temperatures. Part II. The Curve for Sodium Cyanide.*

By CHRISTOPHER KELK INGOLD.

IN Part I of this series (I., 1922, 121, 2419) evidence was given that the equation

$$R \log_e p = J_1 - L_1/T + \alpha \log_e T + \beta T \quad (i)$$

does not correctly represent the form of the vapour pressure curve at high temperatures. There appeared to be two possible causes * of the discrepancy, (a) that the gas laws $pv = RT$ are not applicable to the saturated vapour, (b) that the latent heat of vaporisation is not accurately a quadratic function of the temperature, and an attempt was made to show the operation of cause (a) alone by examining the form of the curve for an element (lead) which is known to yield a monatomic vapour. Reasons were given for supposing that in such a case the latent heat would be a quadratic function of temperature, so that discrepancies could, with certain reservations, be attributed to cause (a). On the other hand, in the case of a polyatomic substance a large increase in the effect of cause (b) is to be anticipated if its influence on the form of the curve is of a measurable order.

The present paper, therefore, contains an examination of the curve for a triatomic compound (sodium cyanide) of about the same order of volatility as lead.

The method of testing the formula was the same as that used previously, the experimental range being divided into the equal intervals, 800—1080° and 1080—1360°, and the observations in each interval plotted on squared paper (Figs. 1 and 2). Smooth curves were drawn through each set of points, and from the curve within the first interval fixed points were chosen from which the constants of an equation of type (i) could be calculated. The equation was

$$\log_{10} p = 5.788 - 9989/T - 1.733 \log_{10} T - 0.00175T \quad (ii)$$

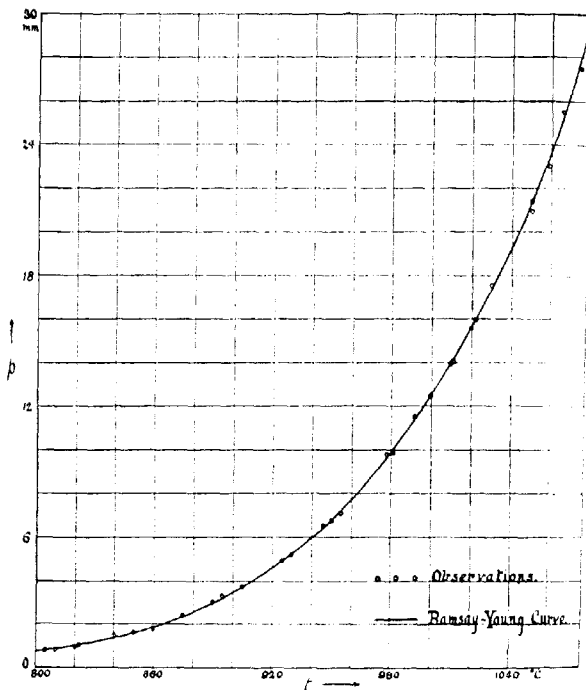
and its graph fits over the smoothed curve of the experimental results within the lower temperature range to an approximation of $\pm 2^\circ$. In the second temperature interval, however, the curve

* Since the Nernst Heat Theorem is not utilised in developing equation (i), which is merely an integrated form of the well-known differential equation of Clausius and Clapeyron, it is perhaps scarcely necessary to point out that the fundamental hypotheses of that theorem can contain nothing which in any way contributes to the discrepancy referred to.

of equation (ii) runs quite away from the experimental points, the difference at the upper end of the range amounting to 50° in the temperature (Fig. 2).

In the case of lead, a divergence was obtained, which, although quite definite and measurable, was small. In the present instance, however, the deviation is large, approximately ten times that observed in the case of lead, and far exceeds any possible error of

FIG. 1.



experiment. Hence, so far as it goes, the evidence is strongly in favour of the view that, in the case under discussion at least, cause (b) is the principal reason of failure of the Nernst equation.

In view of this large discrepancy, it is the more remarkable that (as with lead) the experimental results can be expressed with great accuracy by Ramsay and Young's empirical relation

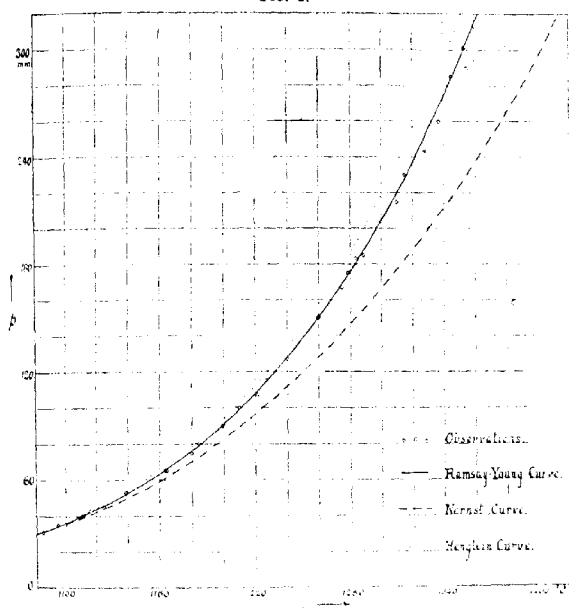
$$T_1/T_2 = m + nT_2 \quad \dots \quad (iii)$$

where T_1 and T_2 are the absolute boiling points of two liquids under the same pressure. Applying the same extrapolation test, mercury being the reference liquid, the constants obtained from the first temperature interval gave the equation

$$T_{\text{NaCN}}/T_{\text{Hg}} = 2.599 + 0.00033 T_{\text{Hg}} \quad \text{. (iv)}$$

the graph of which, within the second interval, is shown by the full line of Fig. 2. (In Fig. 1, it coincides completely with the curve of

FIG. 2.



smoothed results from which the constants were obtained.) There seems to be a slight systematic deviation from the observed values at the highest temperatures used, but, even if this is real, it is very small and is scarcely within the limits of possible measurement. The point must remain to be settled when the observations have been extended to still higher temperatures.

Henglein's relation

$$\log T_1 = a \log T_2 + b \quad \text{. (v)}$$

was subjected to a similar extrapolation test. The formula

$$\log_{10} T_{\text{NaCN}} = 1.045 \log_{10} T_{\text{Hg}} + 0.319 \quad \text{. (vi)}$$

calculated from the curve of Fig 1, gave for the second temperature range a curve (dotted in Fig. 2) which deviated notably from the experimental results, although not so much as the Nernst curve, and in the opposite direction.

Evidently Ramsay and Young's formula is the only one of those investigated which is in the least degree trustworthy for extrapolation. Equation (iv) gives for the boiling point under atmospheric pressure the value 1495° , which may possibly be slightly below the true boiling point if the small deviation referred to above is real. In any event, the rounded value, $1500^{\circ} \pm 10^{\circ}$, is probably trustworthy.

The molecular latent heat, calculated from the curve of smoothed experimental results, amounts to 37,000 cal., which may be taken as correct to two significant figures.

EXPERIMENTAL.

Preparation of Sodium Cyanide.—The material required was prepared from pure hydrocyanic acid and pure carbonate-free sodium hydroxide made from sodium, the evaporation being conducted in in good vacuum. It contained upwards of 99.8 per cent. of sodium cyanide.

Boiling Tubes.—Carbon tubes were used for the final experiments, although moderately good results were obtained with silica tubes coated internally with silicon. It was found that the carbon tubes disintegrated rapidly if fused sodium cyanide was allowed to penetrate them and then solidify. At the end of an experiment, therefore, the fused sodium cyanide was poured out, and the empty tube immediately reheated to volatilise the last traces. An increase in the life of the tubes was thus secured.

Method of Experiment.—The method of making the measurements was generally similar to that employed in the preceding series of experiments (*loc. cit.*), but it was found that owing to the small leakage which inevitably occurs when carbon tubes are evacuated and heated, a small amount of carbon monoxide usually entered during an experiment and converted some of the sodium cyanide into sodium carbonate (Ingold and Wilson, T., 1922, 121, 2273), thus introducing a soluble, but comparatively non-volatile, impurity. In order to avoid error due to this cause, it was necessary (a) to carry out determinations as quickly as possible, using a fresh specimen for every few experiments, and (b) to analyse the material after each experiment. Vapour pressure measurements were not accepted as trustworthy unless the material poured out from the tube contained at least 99.5 per cent. of sodium cyanide. It will be shown on p. 891 that the total pressure curve for a mixture of

sodium cyanide and sodium carbonate is approximately linear, whence it follows that the presence of 0.5 per cent. of sodium carbonate dissolved in the sodium cyanide would lower the vapour pressure by about 0.5 per cent., which would be equivalent to introducing an error of 0.3° to 0.6° into the measurement of temperature. This is considerably less than the error inherent in an individual determination ($\pm 1.4^\circ$ on the average), and is also less than the degree of approximation ($\pm 1^\circ$) to which the curve of smoothed results is believed to be trustworthy.

TABLE I.

<i>p</i> (mm.).	<i>t</i> (obs.).	<i>t</i> (calc.).	Diff.	<i>p</i> (mm.).	<i>t</i> (obs.).	<i>t</i> (calc.).	Diff.
b 0.80	805°	803°	+2°	a 27.5	1075°	1073°	+2°
a 0.85	810	807	+3	b 31.2	1085	1087	-2
b 1.00	820	817	+3	a 35.0	1095	1097	-2
a 1.05	822	820	+2	b 40.0	1111	1110	+1
b 1.50	840	842	-2	a 44.6	1125	1123	+2
a 1.65	850	849	+1	b 52.8	1139	1141	-2
b 1.85	860	858	+2	a 65.2	1164	1164	0
a 2.40	875	876	-1	b 64.7	1165	1163	+2
b 3.00	890	891	-1	a 75.0	1180	1179	+1
a 3.30	895	897	-2	b 80.0	1185	1187	-2
b 3.70	905	905	0	a 90.2	1200	1200	0
a 4.90	925	928	-3	b 100	1210	1211	-1
b 5.20	930	931	-1	a 107	1221	1220	+1
a 6.50	946	948	-2	b 115	1227	1228	-1
b 6.75	950	950	0	a 127	1240	1240	0
a 7.10	955	956	-1	b 150	1260	1260	0
b 9.80	978	980	-2	a 151	1261	1261	0
a 9.90	981	982	-1	b 167	1275	1274	+1
b 11.5	992	993	-1	a 175	1279	1280	-1
a 12.5	1000	1001	-1	b 183	1284	1286	-2
b 14.0	1010	1010	0	a 185	1289	1287	+2
a 14.1	1011	1011	0	b 215	1310	1307	+3
b 15.6	1020	1020	0	a 230	1315	1316	-1
a 16.0	1022	1022	0	b 243	1328	1324	+4
b 17.5	1030	1031	-1	a 260	1337	1333	+4
a 21.0	1050	1049	+1	b 285	1345	1346	-1
b 21.4	1050	1050	0	a 290	1355	1349	+6
a 23.0	1059	1059	0	b 301	1353	1353	0
b 25.5	1066	1066	0				

Table I contains the results of fifty-seven determinations. In the first column, "a" denotes that the measurement was one of a series taken in order of ascending pressures, and "b" that it was one of a series in order of descending pressures. The pressures are believed to be correct to 0.1 mm. (where a decimal is quoted), but it was attempted to read them to 0.05 mm. The observed temperatures (second column) could be read in the instrument used to 0.1°, but are quoted to the nearest one degree. The third column gives the temperatures calculated from formula (iv) and Smith and Menzies's data for mercury (*J. Amer. Chem. Soc.*, 1910, 32, 1447), and the fourth column the differences, the algebraic

average of which is -0.06° , that is, nearly zero, as it should be. Their average, disregarding the sign, is 1.4° .

Table II exhibits the smoothed results for every 10° , from 800° to 1360° . Intermediate values can be obtained to the nearest one degree by linear interpolation. The pressures are probably correct to 1 per cent., and the temperatures to one degree.

TABLE II.

t .	p (mm.).	t .	p (mm.).	t .	p (mm.).	t .	p (mm.).
800°	0.76	940°	5.80	1080°	29.4	1220°	107
810	0.90	950	6.60	1090	32.4	1230	117
820	1.06	960	7.52	1100	36.0	1240	127
830	1.25	970	8.55	1110	39.8	1250	138
840	1.45	980	9.70	1120	43.7	1260	150
850	1.67	990	11.0	1130	47.7	1270	162
860	1.92	1000	12.4	1140	52.2	1280	175
870	2.22	1010	14.0	1150	57.6	1290	189
880	2.55	1020	15.6	1160	63.0	1300	204
890	2.96	1030	17.3	1170	69.0	1310	220
900	3.43	1040	19.2	1180	75.6	1320	237
910	3.95	1050	21.3	1190	82.5	1330	255
920	4.50	1060	23.7	1200	89.8	1340	273
930	5.10	1070	26.4	1210	98.3	1350	293
						1360	314

TABLE III.

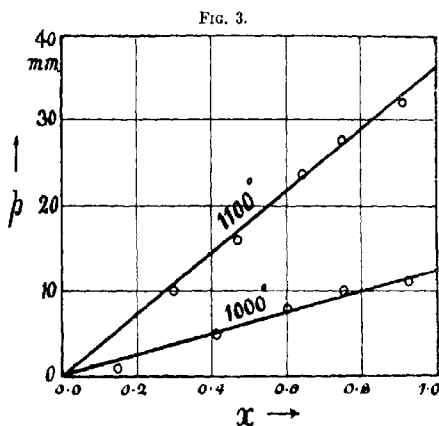
p (mm.).	t (obs.).	t (Nernst).	Δ_N .	t (Henglein).	Δ_H .
0.76	800°	802°	+ 2°	801°	+ 1°
1.20	828	829	+ 1	828	0
1.85	857	858	+ 1	857	0
2.81	886	886	0	885	- 1
4.18	914	913	- 1	913	- 1
6.10	943	942	- 1	942	- 1
8.76	973	971	- 2	973	0
12.4	1000	999	- 1	1000	0
17.2	1029	1029	0	1029	0
23.6	1059	1060	+ 1	1058	- 1
32.0	1089	1090	+ 1	1088	- 1
42.8	1118	1122	+ 4	1116	- 2
56.6	1148	1155	+ 7	1144	- 4
74.1	1177	1187	+ 10	1172	- 5
95.9	1207	1220	+ 13	1202	- 5
123.0	1236	1254	+ 18	1230	- 6
156.3	1266	1290	+ 24	1260	- 6
196.8	1295	1328	+ 33	1287	- 8
245.8	1325	1367	+ 42	1315	- 10
304.7	1355	1405	+ 50	1345	- 10

In Table III, the experimental results are compared with the values calculated from the Nernst and Henglein formulæ. The first column records pressures and the second temperatures calculated by the Ramsay-Young formula (iv), these values being practically identical with those read from the curve of smoothed results. The third column shows the temperatures calculated by formula (ii) to correspond with the pressures given in the first column, and the fourth column the differences between these temperatures

and the corresponding temperatures of the second column. The temperatures given by formula (vi) are shown in the fifth column, whilst the last column gives the differences between these and the figures of the second column.

Supplementary Note: The Total Pressure Curve for Mixtures of Sodium Cyanide and Sodium Carbonate.

The following table records the total vapour pressures of mixtures of sodium carbonate and sodium cyanide at two temperatures, $1000^\circ \pm 1^\circ$ and $1100^\circ \pm 1^\circ$. x = Mols. of NaCN/[mols. of NaCN +



2 (mols. of Na_2CO_3)]. The composition of the material was determined by analysis after each vapour pressure determination. The accompanying curves (Fig. 3) show that the total pressure is a nearly linear function of the molecular composition of the mixture, and that the vapour pressure of sodium carbonate is negligible in comparison with that of sodium cyanide at the temperatures investigated.

Temp. $1000^\circ \pm 1^\circ$.		Temp. $1100^\circ \pm 1^\circ$.	
x .	p (mm.).	x .	p (mm.).
0.00	0.0	0.00	0.0
0.16	1.0	0.30	10.0
0.41	5.0	0.47	16.2
0.60	7.8	0.64	23.6
0.75	9.9	0.75	27.6
0.92	11.1	0.91	32.0
1.00	12.4	1.00	36.0

CVII.—*Anodic Formation of a Perchloride of Manganese.*

By ALAN NEWTON CAMPBELL.

IN the course of some experiments on the cathodic deposition of manganese from chloride solution, the solution round the anode, which was separated from the main body of the liquid by a porous pot, was observed to have assumed a deep, almost black, colour. On examination against a strong light it was seen to be a very deep red, but quite clear solution. It was thought that this solution might be analogous to the dark liquid obtained by Scheele, by treating manganese dioxide with cold concentrated hydrochloric acid, the constitution of which has never been definitely settled. On the other hand, it might be a colloidal solution of manganese dioxide, since manganese dioxide is always formed during the electrolysis of manganese salts, even of the chloride, when the acid concentration is low ($\text{Mn}^{++} + 2\text{H}_2\text{O} + 2\oplus = \text{MnO}_2 + 4\text{H}^+$). Reference to the literature revealed the fact that higher oxidation salts of manganese have been prepared anodically, namely, $\text{H}_2\text{Mn}_2(\text{SO}_4)_4 \cdot 8\text{H}_2\text{O}$ (Foerster, "Elektrochemie wässriger Lösungen," 1915 edn., p. 742) and manganic nitrate (*Z. anorg. Chem.*, 1910, **68**, 1607), but no information as to a higher chloride was obtainable.

EXPERIMENTAL.

The dark coloured solution was prepared in the following way. The electrolysis cell consisted of a rectangular glass jar containing a porous pot. The porous pot contained the anolyte of 3*M*-manganous chloride, to which an equal volume of concentrated hydrochloric acid had been added, and the main body of the cell the catholyte of ammonium chloride, containing 250 grams of the salt per litre. Both anode and cathode were sheets of platinum foil. An anodic current density of 6 amp./sq. dem. was used, corresponding to a total current of 6 amperes. Current was passed for two and a half hours, during which time the temperature rose from 18° to 47°. Rise of temperature, however, had previously been found to be not prejudicial to the process. On the other hand, neither current density nor manganese concentration can be much reduced. The clear anolyte was then examined under the ultra-microscope, but no colloidal particles were discernible. It was therefore thought that the dark colour must be due to the presence of a higher chloride of manganese.

For purposes of comparison, Scheele's dark liquid was prepared by allowing concentrated hydrochloric acid to stand over-night

in contact with finely powdered manganese dioxide. After filtering, a dark liquid was obtained which was quite clear and showed the same dark red colour as the anodic product. This liquid deposited manganese dioxide on dilution, a property also possessed by the anodic product. It seems, therefore, as if both liquids contain the same higher chloride. Moreover, as the prevailing colour of quadrivalent manganese salts is given as brown (red?) and that of the tervalent salts as violet (compare Foerster, *loc. cit.*), a first assumption was made that the chloride was, mainly at all events, the tetrachloride.

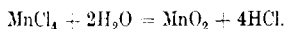
Before analysing the anodic product, free chlorine was removed. This was readily and completely brought about by bubbling nitrogen through the liquid. Removal of the free chlorine produced no change in the liquid.

The analysis was carried out by two methods. Ten c.c. of the dark solution were mixed with 10 c.c. of *N*/10-ferrous sulphate, syrupy phosphoric acid was added, and the excess of ferrous sulphate titrated with standard potassium permanganate. The dark colour disappeared completely on the addition of the ferrous sulphate. The reaction was assumed to be



This determination gave as the concentration of manganese tetrachloride, 0.0185 gram-mol. per litre.

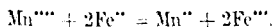
Twenty c.c. of solution were boiled with excess of water, and the precipitated manganese dioxide was filtered, ignited to Mn_3O_4 , and weighed. Here the reaction was assumed to be



The concentration of manganese tetrachloride found by this method was 0.0188 gram-mol. per litre.

It will be observed that, on the assumption that the manganese is in the quadrivalent condition, very good agreement is obtained between the two methods. On the assumption of tervalent manganese, no such agreement is obtained. This indicates strongly that the higher chloride present is entirely the tetrachloride.

Another portion of the liquid after removal of free chlorine was placed in a porous pot, standing in a beaker containing a mixed solution of *M*-ferrous sulphate and *M*-ferrie chloride. Indifferent electrodes of platinum were inserted in both liquids and the *E.M.F.* of the combination was determined by the compensation method. The equation corresponding to this potential difference is



H H*

The potential difference is therefore given by the expression

$$E = E_{\text{Mn}^{+++}/\text{Mn}^{++}} - E_{\text{Fe}^{+++}/\text{Fe}^{++}} + \frac{0.058}{2} \log \frac{[\text{Mn}^{+++}][\text{Fe}^{++}]^2}{[\text{Mn}^{++}][\text{Fe}^{+++}]^2},$$

where $E_{\text{Mn}^{+++}/\text{Mn}^{++}}$ = normal potential of manganic (quadrivalent)-ions in presence of manganous-ions, and $E_{\text{Fe}^{+++}/\text{Fe}^{++}}$ = normal potential of ferric-ions in presence of ferrous-ions. The other symbols have their usual significance. The value obtained for the first determination was 0.663 volt (at 16°). We therefore have

$$0.663 = E_{\text{Mn}^{+++}/\text{Mn}^{++}} - 0.750 + \frac{0.058}{2} \log \frac{[0.0187][1]^2}{[1.5][1]^2};$$

whence $E_{\text{Mn}^{+++}/\text{Mn}^{++}} = 1.468$ volts (hydrogen scale).

The manganese solution was now diluted with three times its volume of 1.5*M*-manganous chloride solution, and the *E.M.F.* again determined. This was found to be 0.639 volt at 16°. Here we have

$$0.639 = E_{\text{Mn}^{+++}/\text{Mn}^{++}} - 0.750 + \frac{0.058}{2} \log \frac{[0.0047][1]^2}{[1.5][1]^2};$$

whence $E_{\text{Mn}^{+++}/\text{Mn}^{++}} = 1.462$ volts (hydrogen scale).

Taking the mean of these two values, we obtain as the normal potential of quadrivalent manganese-ions in presence of bivalent manganese-ions, 1.465 volts (hydrogen scale) at 16°.

The amount of tetrachloride present being so small in comparison with the amount of manganous chloride, it was thought that any attempt to crystallise it out would have been fruitless.

In conclusion, it may be mentioned that the tetrachloride is sensitive to light, particularly ultra-violet light, the solution losing its dark colour and giving off chlorine gas, without, however, any precipitation occurring.

Summary.

1. A solution of a higher chloride of manganese, similar to Scheele's dark liquid, has been prepared anodically.
2. The solution has been analysed and shown to contain only the tetrachloride, MnCl_4 , apart from unchanged manganous chloride.
3. The normal potential of quadrivalent manganese-ions in presence of bivalent manganese-ions has been calculated from oxidation-reduction potential measurements.

In conclusion, the author wishes to acknowledge his indebtedness to Professor A. J. Allmand for some very valuable suggestions.

KING'S COLLEGE, STRAND, W.C.

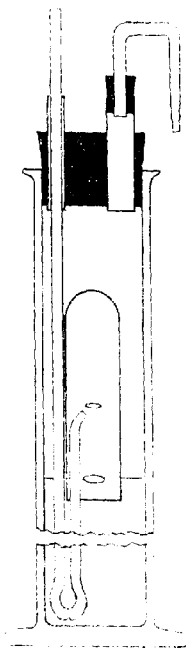
[Received, March 29th, 1923.]

CVIII.—*Mercury Cleansing Apparatus.*

By AUGUSTUS EDWARD DIXON and JAMES LYTTLE MCKEE.

ALTHOUGH embodying no new principle, the form of mercury cleaner represented in the accompanying diagram has been found serviceable and convenient in use.

The mercury is contained in a cylindrical jar, 39 cm. high and 5 cm. in bore, the mouth of which is closed by a rubber bung carrying two tubes: of these, one is a sleeve about 6 cm. long and just wide enough to pass the long leg of a U-tube; the other, about 15 mm. in bore, is provided with a rubber stopper and bent tube for connexion with the pump. This U-tube, the essential part of the apparatus, is bent as shown: its bore may be from 2.5 to 2.7 mm., and to minimise the risk of fracture in handling, it should be fairly thick-walled—say, 6 mm. in external diameter. At the bottom of the U-bend, a hole is blown. Entering through this hole, the mercury is caught in an air current, developed by suction (or by pressure), is swept by it up the short leg of the tube, and from the nozzle of the latter is delivered in a spray of minute droplets, which strike against the wall of a glass jacket. Thence the comminuted mercury falls back into the mass of liquid, the circulation being continuous and complete. For the long leg of the U—the “air inlet tube”—a suitable length is 45 cm.; the short leg, or “spray tube,” should be long enough for its conical nozzle (constricted at the end to a diameter a little more than one-half that of the main bore) to stand at about 4 to 5 cm. above the surface of the mercury, when the inlet hole for the latter is just at the bottom of the jar. This inlet hole has a diameter about the same as the tube-bore; its everted edge should be filed off, or else very lightly fused, lest any thickening should impede the entrance of the mercury. Surrounding the air inlet tube and its sleeve is an air-tight collar



of thick-walled rubber tube, smeared internally with glycerol, in order that the U-leg may be slid up and down easily.

To prevent the mercury from splashing over the wall of the jar, and thus escaping from circulation, the spray tube is covered by a jacket, floating in the mercury, and long enough for its top to clear the nozzle by 4 or 5 cm.; as a rule, a length of about 10 cm., overall, is sufficient. It should be at least 25 mm. in bore, and 1 to 1.5 mm. thick in the wall: between the legs of the U-tube, there must be space enough for the jacket to move freely up and down without being pinched. Through its wall, exactly at the mercury level, as the jacket floats, a large slot is cut, crosswise (by means of a round file, lubricated with turpentine), not less than 15 mm. long; 3 cm. above this, another slot is filed, only some 3 to 4 mm. long. The point for the lower slot may be found by hanging the jacket, mouth downwards, on the short leg of an open U-tube, and lowering the system until the jacket floats, upright, in the mercury; there should be free communication between the mercury surface, outside, and that inside the jacket.

To operate the machine, the procedure is as follows. A suitable charge of mercury having been poured into the jar, the jacket is slipped over the spray tube, the slots being turned so as nearly to face the air inlet tube. The latter having been slid well up in its sleeve, the rubber bung is pushed home, air-tight, the sprayer now being slid down until the U-bend is felt to touch the bottom of the jar; then (unless it springs up of itself), it is drawn up just clear. The pump is started, and when spraying is established, the air inlet tube is slightly rotated in its collar, so as to direct the flying mercury obliquely against the wall of the jacket. Thereupon, if the mercury is rather foul, a stream of infinitesimal globules—almost a dust—travelling at high speed, ascends the jar in a grey spiral, attains a certain height, and thence descends in a somewhat wider spiral; viewed across the jacket, the direct and reversed spirals form a sort of "figure-of-eight." With a nearly clean sample, however, it is different, the ejected particles now coalescing so readily that, soon after striking the wall of the jacket, they collect into beads, heavy enough to trickle down.

Very foul mercury—especially when zinc is the contaminant—develops a black "froth," containing much mercury and so voluminous that it may soon fill the jacket. To defeat its formation, the mercury is covered with a layer of dilute nitric acid (1 vol. of concentrated acid in 20 vols. of solution), not deep enough to flood the upper slot in the jacket. At first, the contaminant metal alone passes into solution, a few drops of the acid liquor, withdrawn by means of a pipette, yielding with alkali hydroxide a corresponding

reaction; later, the reagent gives a copious black precipitate. The mercury is now washed, roughly dried, filtered, and the purification completed by "dry blowing."

For an apparatus of the dimensions named, about 250 c.c. of mercury is a convenient charge. More, or less, of course, may be taken, if the length of the spray tube is adjusted to suit; at very deep or very shallow immersions, however, the conditions for producing a steady and well comminuted spray are obviously not the same as those at an intermediate depth.

A few minor details may be added. (i) Plugs of mercury in the spray tube may not be ejected readily when the pump is started, air bubbling out, instead, at the mercury inlet hole. If so, the air inlet is closed for a few seconds by the finger; on its removal, the burst of air will force out the plugs, and spraying will follow. (ii) By putting over the air inlet a test tube, packed loosely with cotton wool about a central tube, running the full length of the test-tube, the chattering noise may be silenced. (iii) The black deposit that forms inside the spray tube is removable by a dip into sulphuric acid-"dichromate" mixture, followed by rinsing with water and then alcohol: the tube need not be dried afterwards.

Apart from its compactness, stability, and general strength, the foregoing apparatus has the merit of requiring practically no attention while running. In a particular test-experiment, 3.5 kilos. of mercury, fouled with zinc (1 in 5000), after three hours' wet blowing had become almost free from "drag": it was then dry blown for eight hours, at a venture, the filtered product, when sprayed for another hour, showing no surface tarnish. At this stage, it passed all the usual tests, and when used in a concentration cell with dilute sulphuric acid against highly purified mercury, failed to stir the needle of a meter, reading directly to millivolts. After a further run of sixteen hours, although the mercury surface was scarcely dimmed, a perceptible dark scum had formed inside the spray tube.

With a wider jar, and a trifling modification of the jacket, to permit the use of a relatively large volume of the supernatant solution, this apparatus would probably be suitable for the purification of mercury by Bettel's cyanide method (*Chem. News*, 1908, 97, 158).

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[Received, March 26th, 1923.]

Some Constitutional Problems of Carbohydrate Chemistry.

A LECTURE DELIVERED BEFORE THE CHEMICAL SOCIETY ON
FEBRUARY 22ND, 1923.

By JAMES COLQUHOUN IRVINE, C.B.E., F.R.S.

I FEEL that an honour has been done to my research school in inviting me to lay before this Society an account of some of the studies upon which we have been engaged, but my gratification is tempered by the sobering thought that the title of this lecture is ill-chosen.

No rapid survey can be made, no adequate synopsis can be given, of the manifold problems of carbohydrate constitution which have already been solved or which still await adequate representation. To discuss even in broad outline the structure of a single sugar demands the consideration of a bewildering series of reactions and relationships, and to deal, in one lecture, with all classes of carbohydrates is to court disaster. My excuse in attempting what I believe to be the impossible is that, to me, the carbohydrates are among the most important, the most baffling, yet withal the most fascinating substances which engage the attention of the chemist.

To the student who brings to bear on our science the special appreciation which comes from tracing historical developments there must be abundant satisfaction in discerning how our knowledge of carbohydrates has expanded in response to the stimulus conveyed by fresh views on structure. The pioneer researches, and early explorations of the fate of carbohydrates in the living organism, must not be passed over lightly; the experimental difficulties encountered to-day serve but to remind us of the skill and patience devoted to this work. Yet, go back rather more than a century and you will find the "Old Masters" struggling with the sugars and giving in a few lines of print all that was then known regarding them. Bridge a gap of seventy years from their time and you will find little in addition: a few more sugars had been recognised and a greater variety of derivatives had been prepared, but, in the absence of structural views, the information provided is purely descriptive and empirical. Then began that brilliant period of constitutional carbohydrate chemistry which culminated in the great awakening we owe to Emil Fischer.

It was indeed a marked advance to be able to expand the formula $C_6H_{12}O_6$ so as to display, not only the significant groups, but also

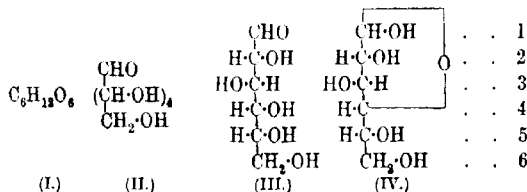
their configuration, and thereby to account for the isomerism and mutual relationships of the simple hexoses. Almost inevitably this progressive phase was followed by a resting stage, and it is not surprising that, during the past twenty-five years, the study of sugars has shown alternations of activity and stagnation. The present is a period of revival, and, in sympathy with this growing interest, one is tempted to include many aspects of carbohydrate constitution, but with the time at my disposal it seems prudent to confine myself almost exclusively to problems which have engaged the attention of my co-workers and of my colleagues.

Although with the information now available an elaborate classification of carbohydrates is possible, we may, in the interests of simplicity, adhere to the present system and may divide them into three groups:

- (a) Reducing sugars which are unaffected by hydrolysis.
- (b) Glucosidic compounds which, on hydrolysis, yield at least one reducing sugar. (Di- and *n*-saccharides may be regarded as special examples of this class.)
- (c) Polysaccharides.

The above groups are interrelated, and the constitutional problems presented by glucosides, *n*-saccharides, and polysaccharides are obviously dependent on the structure of the simple reducing sugars. Lack of knowledge of the monosaccharides is at once reflected in the complex saccharides.

In order to arrive at the fundamental aspects of carbohydrate structure, we may consider the special case of glucose, and may trace the stages through which our present views regarding the hexose molecule have evolved. These stages are expressed in historical sequence in the scheme shown below, which displays the transition from an empirical formula to the butylene-oxide representation of α - and β -glucose now in general use.



The cyclic formula for reducing sugars has proved of real service, and its adoption has been justified, but it is necessary to point out that, until recently, less than one-half of the molecular archi-

ture of glucose had been studied. When we remember that position 1 in the above formula plays a part in mutarotation, in the formation of glucosides, and in oxidation processes, it will be agreed that this particular alcohol group has placed no obstacles in the way of thorough investigation. The properties of the group indexed as position 2 are not so well defined, but are revealed to a limited extent in the formation of osazones, whilst our knowledge of the group in position 6 is restricted to a few reactions such as oxidation to saccharic acid and the formation of dibromo-derivatives. Speaking generally, however, it may be claimed that the essential reactions of the three hydroxyl groups specified are already known.

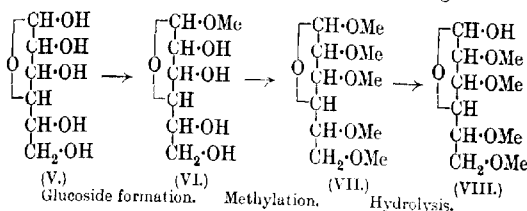
On the other hand, the asymmetric systems indexed as 3, 4, and 5 represent areas in the sugar molecule which had remained almost entirely unexplored. There are good reasons for this gap in our knowledge, yet a proper understanding of the glucose molecule cannot be obtained if, as is generally the case, attention is focussed exclusively on the reducing group; each hydroxyl group must be studied, for each possesses its own particular properties and contributes to the reactions of the molecule as a whole. This consideration leads directly to another point, which I believe to be of even greater importance. It is evident that the linkage of the ring-forming oxygen atom in the molecule need not remain exclusively in one position, but may connect different pairs of carbon atoms, and thus, all the groups from 1 to 6 must be regarded as variables. For example :

- Position 1 may possess either the α - or β -configuration.
- Position 2 may be involved in an ethylene-oxide ring.
- Position 3 " " " a propylene-oxide ring.
- Position 4 " " " a butylene-oxide ring.
- Position 5 " " " an amylene-oxide ring.
- Position 6 " " " a hexylene-oxide ring.

It follows, therefore, that if we include an aldehydic variety, *d*-glucose may react in any one of eleven forms or as a mixture of these isomerides. These complicated possibilities must be taken into account in speculating on the reactions of the so-called "simple" sugars, in tracing their origin, their metabolism, and their relationship to the di- and poly-saccharides.

These are preliminary considerations, and I turn now to an account of how the intimate structure of carbohydrates has been advanced through the agency of one particular method of inquiry, which, for reasons already given, was applied in the first instance to the monosaccharides. I refer to the process of methylation,

a reaction which has been employed to introduce stable methyl groups into all the hydroxyl positions of reducing sugars or into any hydroxyl groups which remain unsubstituted and exposed in a sugar derivative. Taking an example which has been very fully studied, the sequence of typical operations leading to a fully methylated glucose may be expressed by the following scheme :



The first stage is the formation of methylglucoside, a reaction which has the effect of protecting the reducing group, and this is followed by the introduction of methyl groups into the remaining hydroxyl positions. It is important to note that acid hydrolysis of the methylated glucoside affects the molecule only in one position, the glucosidic alkyl group being eliminated, whilst the remaining methyl groups survive. In the tetramethyl glucose thus produced, four hydroxyl groups have been masked, and it is thus possible to study the properties of the reducing group in the absence of many complicating factors. Extending the above principles, it will be clear that if a sugar is substituted by any group or groups capable of subsequent removal by hydrolysis, it is possible to methylate the unoccupied hydroxyl positions and ultimately to obtain definite partly methylated sugars. In these products, the position of the OH groups coincides with the position in which the substituting groups were attached to the original sugar residue. For example, starting from benzylidene methylglucoside, only two hydroxyl groups are available for methylation, and consequently, on completing the series of reactions, the final product obtained was a dimethyl glucose. Reference to the published papers will show that the method is of wide application, and that a large variety of completely and partly methylated aldoses and ketoses have been prepared and examined.

In general, it may be said that alkylated sugars are extremely suitable for exact and critical experimental study. In many cases the compounds crystallise readily in highly characteristic forms and, in addition, the sugars or their glucosides can be effectively purified by distillation in a high vacuum. Moreover, the presence of the alkyl groups increases the solubility in organic solvents

enormously, and thus the reactions of the compounds can be studied under a variety of conditions. Characterised by properties such as I have described, alkylated sugars are well adapted as reference compounds, in that they can be isolated and identified with certainty, even when only small quantities are available. The same remark applies to the alkylated sugars which are liquids, as, in the majority of cases, they yield crystalline anilides or glucosides upon which characteristic physical constants may be determined accurately.

I have referred to the opportunities afforded by alkylated sugars to restrict the attack of reagents to a limited number of selected hydroxyl groups, but a more obvious application of these compounds, and one which is superficially of more importance, lies in the use which has been made of them to solve the structure of typical glucosides, disaccharides, and polysaccharides. If we ascribe to any sugar derivative the general formula $S-G$, where S is a sugar residue and G the group with which it is condensed, then methylation followed by hydrolysis will give as a minimum two products, one of which will be a methylated sugar. Determination of the number and distribution of these methyl groups in each of the cleavage products gives the complete structure of the parent compound, as the mode of attachment of the individual constituents is thereby revealed.

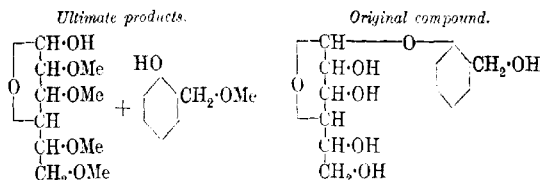
In the special case where the group G is also a sugar residue, the compound under consideration would be a disaccharide, and the general formula may be written $S-S_1$. Precisely the same structural study can evidently be applied to it, with the single difference that two methylated sugars will be obtained on hydrolysis in place of one. The method is equally applicable to the general type S_n , which includes polysaccharides.

This exploitation of methylated sugars in solving constitution was recognised at an early period in our work, but the policy was deliberately adopted of postponing such an extension until the standard methylated sugars required as reference compounds had been examined and definite constitutions assigned to them. Once this was done, results have come quickly, and I now propose to refer to the conclusions which have been drawn in a few typical cases selected from the classes into which carbohydrates are divided.

Constitution of Natural Glucosides.

As already explained, the application of the methylation method to α - and β -methylglucoside results finally in the formation of one of the five different forms in which a tetramethyl glucose can exist. The sugar actually obtained is a crystalline solid, easily purified,

and quickly identified by means of its physical constants. The structure assigned to it is that of formula VIII, and, from what has been said, it will be evident that all carbohydrates based on the same structural model as methylglucoside will yield the same variety of tetramethyl glucose. The first case to be investigated was that of sucrose, which may be regarded as a special case of a glucosidic compound. Methylation followed by hydrolysis gave crystalline tetramethyl glucose, thus solving the constitution of the disaccharide so far as the glucose component is concerned. Another example was afterwards furnished by salicin, which was converted into a crystalline pentamethyl derivative, and this, in turn, gave rise to equimolecular proportions of tetramethyl glucose and saligenin methyl ether. From this result the structure of the parent glucoside is at once apparent.

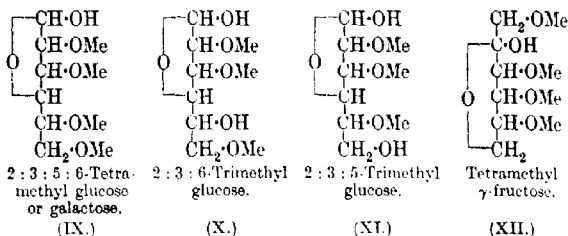


The above proof applies equally to the related glucosides helicin and populin, which must also be derived from the butylene-oxide form of glucose, as they have been prepared from salicin by processes which do not disturb the glucosidic linkage. I may refer also to other results of a similar nature which have recently been obtained with important natural glucosides. It has been shown that the sugar residue in indican and in arbutin has the same linkage as in salicin, whilst amygdalin also falls into line and has been proved to be a glucoside of the type $\text{S}-\text{S}_1-\text{G}$, in which the sugar residue S is similarly capable of yielding tetramethyl glucose. These are not isolated examples, and it is a remarkable fact that all the natural glucosides so far examined yield the stable or butylene-oxide variety of tetramethyl glucose. This result may be translated into the statement that, although glucose can and does exist in a highly reactive form, this variety does not appear to persist in the formation of glucosides in Nature. Reference will be made later to artificial glucosides derived from an unstable modification of glucose, but at this stage it may be stated that such compounds show little tendency, in the absence of hydrolytic conditions, to revert to the more stable isomerides by alteration of the oxygen ring. This change seems, in fact, to be dependent on the presence of the reducing group, and the com-

bined evidence indicates that it is the stable form of glucose which is utilised by plants in the formation of natural glucosides. Some indications exist that the glucosidic components of plant pigments are not invariably derived from a single variety of glucose, but our work in this direction is not sufficiently advanced to permit of a final decision being made.

Constitution of Disaccharides.

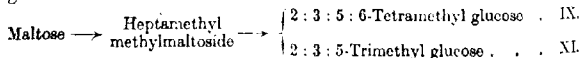
Five methylated hexoses, functioning in the capacity of reference compounds, have served to determine the essential constitution of the most important disaccharides and polysaccharides. The hexoses in question are : tetramethyl glucose, two isomeric forms of trimethyl glucose, tetramethyl γ -fructose, and tetramethyl galactose.



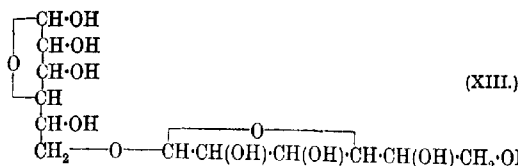
Of these, 2 : 3 : 5 : 6-tetramethyl glucose has proved of greatest service, and it is fortunate that the compound is the most readily identified of all methylated sugars.

In the experimental treatment of reducing disaccharides, the procedure adopted with monosaccharides is followed in that a glucosidic methyl group is introduced before the methylation of the sugar chain is carried out. By a simple, but extremely effective, method these consecutive reactions are conducted in one operation, and in this way a number of fully methylated disaccharides have been obtained. The hydrolysis of these compounds has given results which, as in the examples already quoted, are decisive in displaying the manner in which the hexose components are united. As the principles involved have already been explained, the structural studies of typical disaccharides can be readily synthesised.

Maltose.—The essential steps required in this particular investigation are shown below :

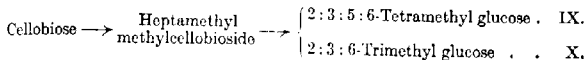


Utilising the structures for IX and XI, the coupling of the glucose residues in maltose is shown to be :

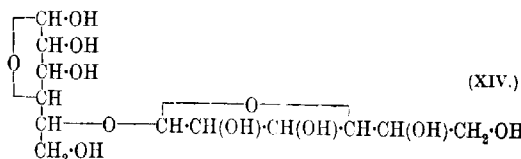


The formula thus established finds application, as will be described later, in deducing the constitution of the starch molecule.

Cellobiose.—An entirely different mode of combining two hexose residues is displayed by cellobiose, as one glucose molecule is attached through its reducing group to the 5-position of the second glucose molecule. This is shown from the sequence of changes :

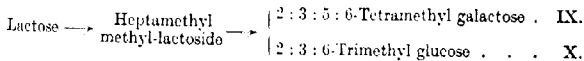


From these results it follows that cellobiose should be represented by the structure :



Apparently the attachment of the hexose molecule depicted in the above formula is characteristic only of natural carbohydrates, as the same coupling is present in cellulose, in starch, and in glycogen, but not in synthetic dextrins. Meanwhile, it is of interest to find that precisely the same condition exists in the disaccharide lactose.

Lactose.—The mutual relationships of the glucose and galactose residues in lactose are at once evident from the experimental scheme :

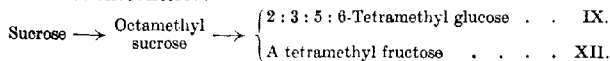


Considering the origin of lactose, it is important to find that the galactose component belongs to the stable type and that the reactive, or γ -form, is definitely absent. This point was readily established, as, although tetramethyl galactose is a liquid, it was identified by conversion into the well-defined crystalline anilide in yields which show that no other isomeride was present.

Taking into consideration the mutual relationships of the compound sugars, the constitution of other reducing disaccharides may be deduced from the results already obtained experimentally,

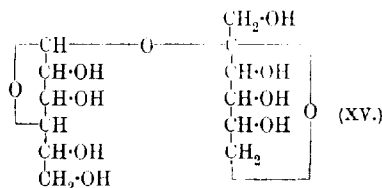
but meanwhile the complicated case presented by sucrose may be discussed.

Sucrose.—So far as two factors are concerned, research on sucrose proved to be comparatively simple. In the absence of a reducing group, the actual methylation presented few difficulties, and tetramethyl glucose, which is one of the scission products obtained from octamethyl sucrose, crystallises readily. Closer inspection of the practical details will, however, reveal some of the obstacles encountered.



The fructose derivative was a liquid, and its separation by distillation proved to be tedious and imperfect. This was overcome by replacing octamethyl sucrose by the corresponding heptamethyl derivative, but another difficulty was then encountered, as the constitution of the tetramethyl fructose was unknown. The compound was, moreover, abnormal, being dextro- in place of lævo-rotatory, and although earlier investigations had already revealed this irregularity, prolonged research has been necessary in order to ascribe a formula to the reference sugar.

It is now recognised that the compound belongs to the type generally known as " γ -sugars," and I hope to refer to these curious isomerides at a later stage. Meanwhile, it may be stated that the normal levorotatory form of fructose has been definitely proved to be a butylene-oxide and that in the tetramethyl fructose now under consideration the internal oxygen ring is displaced to one of the alternative positions. The first suggestion that an ethylene-oxide ring is present is no longer tenable, and in a paper now before the Society a former colleague provides experimental evidence in favour of an amylene-oxide structure. According to this view, the formula for sucrose becomes :



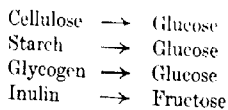
It may be mentioned that both the dimethyl and the trimethyl fructose obtained from inulin are likewise γ -sugars, and contain the same internal ring which is present in the ketose fragment of ^{the} sucrose. The examination of these sugars which is in progress will ^{will} ~~will~~ further light on the structure of sucrose.

From what has been said, it will be admitted that a new complication has been introduced into studies on the inversion of sucrose, as the initial condition of one of the hydrolysis products is transient. The disaccharide thus furnishes an interesting case where methylation reveals a feature of molecular structure which other processes fail to detect.

Polysaccharides.

Although doubtless any reducing sugar is capable of yielding a corresponding polysaccharide, authentic examples of the latter class of compound are not numerous and, up to the present time, our attention has been restricted to the four most important representatives: cellulose, starch, glycogen, and inulin. It is perhaps advisable to express the opinion that we are scarcely justified in claiming that the names used above refer to individual compounds, and, strictly speaking, we should meanwhile regard them as applicable to groups of closely-related compounds.

Systematic study of the polysaccharides on constitutional lines is naturally more difficult than that of the related sugars. The absence of crystalline structure, the inconvenient solubilities involved, and the uncertainty regarding the uniformity of the material under examination are disadvantages, the full measure of which quickly becomes apparent in the experimental treatment of the compounds. These obstacles have not been allowed by chemists to stand in the way of investigating polysaccharides, which have been examined with commendable patience, yet it must be admitted that the reactions available for elucidating constitution are few in number and are difficult to interpret. Above all, the lack of precise information leading even approximately to the molecular weight of members of the group has proved a serious disadvantage. Two fundamental points, however, have long been recognised. The polysaccharides as a class possess the formula $(C_6H_{10}O_5)_x$, and are apparently polymerides of definite molecular units. Although little information can be gleaned from an empirical formula of this nature, the situation becomes clearer when it is remembered that, on complete hydrolysis, each polysaccharide is converted into a monosaccharide. Familiar examples are:

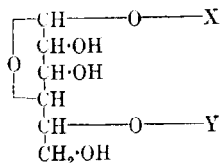


The evidence afforded by hydrolysis is important but, on occasions, may be utterly misleading, and consideration of one example will

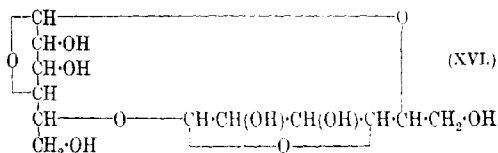
give an indication of the pitfalls which await the investigator in this field. The fact that inulin is converted by the action of dilute acids into the ordinary levorotatory variety of fructose led very naturally to the idea that the polysaccharide is derived from this form of the sugar. Such is not the case, and it is now certain that the fructose molecule liberated when inulin is decomposed is a dextrorotatory ketose, which reverts at once to the stable levorotatory variety. An extreme case, parallel with that of sucrose, has been quoted, but it serves to illustrate the caution which must be exercised in work of this description. Failure to appreciate the complex isomerism of which the monosaccharides are capable has led in other cases to hasty and premature speculation.

Although, from the structural point of view, inulin is the most unique, and, in many respects, the most interesting of the polysaccharides, it is perhaps advisable to deal, in the first instance, with members of the class which are related to glucose. I turn, therefore, to the case presented by cellulose.

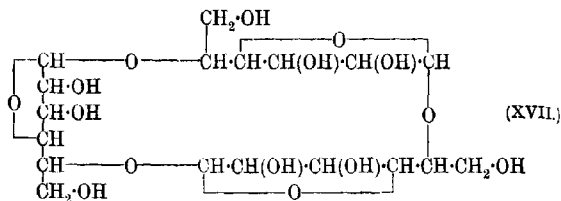
Cellulose.—In a paper now before the Society, results are described from which the constitution of the molecular unit of cotton cellulose may be deduced. To avoid repetition, I shall omit a detailed discussion and confine myself strictly to a synopsis of the essential evidence. Cotton cellulose has been converted into α -methylglucoside in yields which are practically quantitative, so that there can be little reason to doubt that the polysaccharide is composed entirely of glucose units. This result, of course, gives no clue as to the linkage of these glucose residues, but the information has been supplied by a parallel research on fully methylated cellulose. The alkylation proceeds readily up to the dimethyl stage, but thereafter the methoxyl content rises very slowly, and it has been a matter of some difficulty to obtain a trimethyl cellulose and to prove that this product represents the experimental limit of the substitution. Now, it has been known for some years that when dimethyl cellulose is hydrolysed there results a complex mixture of methylated sugars, one component being 2:3:6-trimethyl glucose. This result, significant in itself, justified only one step being taken in ascribing a formula to cellulose, which, in consequence, might be represented by the expression :



Beyond the fact that they must consist of some form of glucose residues, the nature of the groups X and Y remained quite unknown until the fully methylated cellulose I have mentioned was available for hydrolysis. In addition, a further complication was introduced (and the point is somewhat elusive) through lack of any information as to how the hydroxyl groups in cellulose are distributed between the different C_6 units. Applying the considerations already discussed, reflection will show that, according to the manner in which the hydroxyl groups are shared by each C_6 component, a trimethyl cellulose may undergo hydrolysis in four different ways and that, as a maximum, forty-nine methylated sugars may then be produced. These formidable possibilities are dealt with in the paper referred to, but the result actually obtained was the simplest possible of all the alternatives. Trimethyl cellulose was converted quantitatively into 2 : 3 : 6-trimethyl methylglucoside, and this, in turn, yielded the corresponding sugar, unmixed with any isomeride or with any other derivative of glucose. A striking simplicity is thus established for the cellulose molecule, as the unknown fractions X and Y are shown to be identical with each other and with the nucleus glucose residue. In order to expand this result into a molecular structure, it is necessary to know how many of these glucose residues go to form the unit. The question is largely solved when the constitution of cellobiose is taken into account, as good grounds exist for claiming that this sugar is a definite fraction of the cellulose complex. The simplest expression of the cellulose molecule therefore consists of two anhydro-glucose residues connected as under :



Further expansion of the formula is, however, necessary to accommodate the fact that the yield of cellobiose from cellulose does not exceed 50 per cent., and this important condition is satisfied by including three glucose residues in the molecule. There are four different ways of building up such a structure, but three of the formulae thus obtained imply that cellulose should be convertible into other disaccharides in addition to cellobiose. Experimental evidence is, on the whole, against this view, and, as the remaining alternative is free from such an objection, it is meanwhile selected as the most appropriate.



The essential reactions of cellulose are satisfied by the above formula, but in two respects the results furnished by the methylation process fail to complete the architectural scheme of the cellulose complex. No indication is given of the α - or β -configuration of the glucose components, and no idea is conveyed of the mechanism or extent of the polymerisation undergone by the simple molecule. We realise, however, that our work is not at an end, and it may be stated that, by the degradation of esparto cellulose, a compound corresponding to the molecular unit postulated above has already been isolated. Now that the outlines of the cellulose molecule have been defined, many further developments will be apparent, and we are engaged in extending our researches to various forms of modified celluloses.

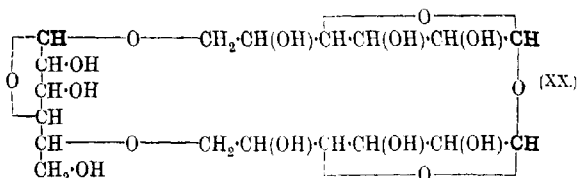
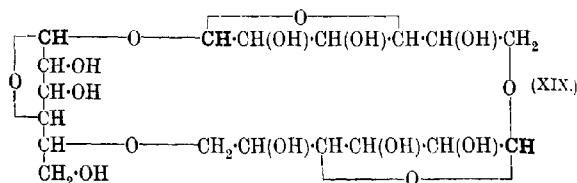
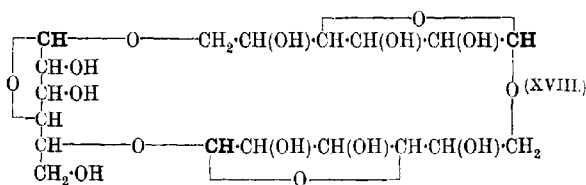
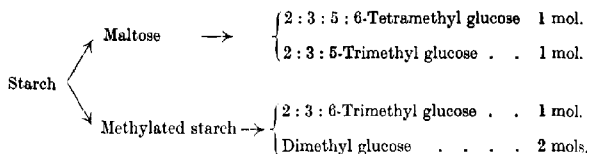
Starch.—Turning to the problem of the constitution of starch, very much the same difficulties emerge as have been referred to in the case of cellulose and, viewed superficially, the two polysaccharides have much in common. Like cellulose, starch is composed entirely of glucose residues and contains three hydroxyl groups for each C_6 unit present in the molecule. It does not follow, although this is almost invariably assumed, that each glucose residue contains three unsubstituted hydroxyl groups, or that the distribution of the three groups is uniform. The primary reaction of starch which, so far as we can tell, must be accommodated in a structural formula is the production of the disaccharide maltose by the action of diastase. Starch is also distinguished sharply from cellulose in being more readily hydrolysed by acids, and this at once points either to

- (1) a different type of polymerisation,
- (2) a different mode of attachment between the individual sugar residues, or to

- (3) a variation in the type of the glucose units.

In other words, part of the starch molecule might conceivably be related to γ -glucose, but this possibility can now be definitely excluded from the results furnished by methylation. These results are in themselves simple, but few reactions impose greater demands on the experimenter than the alkylation of starch.

As a rule, the procedure in methylating compounds of this nature is to use, in the first instance, methyl sulphate as the reagent and, when the methylation has proceeded far enough to render the product soluble in organic solvents, to complete the substitution by means of the silver oxide reaction. In the case of starch, there is clear evidence that these alternative reagents act in a different manner, owing to the preferential attack of silver oxide and methyl iodide on one particular hydroxyl group. The methylation can, in fact, be arrested definitely when a dimethyl starch is the sole product ($\text{OMe} = 32$ per cent.), but by varying the procedure, the methoxyl content can be gradually increased until it reaches the value 37 per cent. It should be stated that this is not an absolute maximum, but represents a second definite stage beyond which further methylation becomes a matter of increasing difficulty. The lower value for methoxyl (32 per cent.) corresponds, as stated, to a dimethyl starch, and no definite structural evidence is forthcoming from the hydrolysis of this compound. On the other hand, the higher methoxyl content (37 per cent.) agrees with the theoretical amount required for an anhydrotrisaccharide, in which three methyl groups are attached to one glucose residue, whilst four such groups are shared by the two remaining glucose residues. The same result has been obtained consistently in different preparations, and ultimate analysis has confirmed the composition. Hydrolysis of this methylated starch shows that this is not a coincidence. The sugars thus produced were isolated in the form of the corresponding methylglucosides and separated by vacuum distillation. Two products were in this way obtained, one being a trimethyl methylglucoside, and the other a dimethyl methylglucoside. It is significant that these products were formed in the molecular ratio of 1:2. On isolating the respective sugars from the compounds, a totally unexpected result was obtained, as 2:3:6-trimethyl glucose was produced from the trimethyl methylglucoside. As will be seen from inspection of formula X, we are forced to the conclusion that in starch one glucose component is linked in a manner which is duplicated in cellulose, cellobiose, and in lactose, but is absent in maltose. Combining these factors, it follows that, as a minimum, the starch molecule must contain three glucose units arranged in such a manner that one pair displays the coupling present in maltose, whilst another pair reproduces the linkage characteristic of cellulose. The results summarised in the scheme given below indicate the conditions which must be satisfied, and these are fulfilled by any one of three formulae.



(Letters in block type designate the potential reducing groups.)

In reviewing the three possibilities, there is no diagnostic reaction which will enable a final decision to be made between them, but the formulæ differ in one important respect. Maltose may be produced in one way only from formulæ XIX and XX, and in two ways from the remaining alternative, which is thus preferred until the completion of work now in progress. The objections which may be offered against the adoption of such a formula have been discussed elsewhere, and the view now expressed receives strong support from the fact that very similar results have been obtained with glycogen.

Glycogen.—In general, it may be said that the methylation of glycogen displays precisely the same features as were encountered

in the case of starch. The reaction shows a distinct tendency to cease at a stage where a dimethyl glycogen is the essential product, but frequent repetition of the alkylation occasions a slow increase in the methoxyl content, which has now been raised to a value close to that required for a trimethyl derivative. In a number of respects, however, minor differences are apparent between methylated starch and methylated glycogen, and these suggest that, although a close parallel exists between the respective molecular units, they may not prove to be identical.

One highly important factor has already been established with certainty, and that is the formation of crystalline 2 : 3 : 6-trimethyl glucose by the hydrolysis of a methylated glycogen containing 37 per cent. of methoxyl. The reaction which gave this result proceeds in exactly the same way as the hydrolysis of methylated starch and points to the idea that an anhydro-trisaccharide represents the glycogen molecule. Consequently both starch and glycogen resemble each other and also cellulose in possessing the unit shown in formula X. Beyond this, it is impossible to speak with certainty at the present time, as the constitution of the other hydrolysis products obtained from methylated glycogen has not been fully developed.

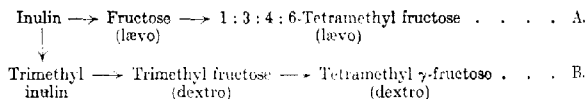
Taking a general view of the three polysaccharides related to glucose, a number of interesting points emerge. The first undoubtedly is their surprising simplicity. In the production of these compounds in nature complications of structure have been avoided, and although in the end there are wide differences between the polymerised aggregates to which we apply the names cellulose, starch, and glycogen, the inner molecular structure is remarkably alike. Apparently the contrasting properties of these polysaccharides are dependent chiefly on the extent and, more particularly, on the mechanism of the polymerisation undergone by the molecules, and we know little or nothing concerning these factors. Analogy is dangerous, but as we are dealing with molecular architecture, I may remind you that many different buildings, varying in design and function, may be erected with bricks of identical material and mould. The analogy may serve to reveal my opinion of the vast problems which have still to be solved before we can trace how, and why, an anhydrotrisaccharide molecule can take up its place as part of a cellulose fibre or of a starch grain.

A second generalisation is that polysaccharides are not complex glucosides in which the groups of one glucose residue are substituted by chains of other glucose residues. Two synthetic dextrans have been shown to conform to this model, but no evidence is

forthcoming that any natural polysaccharide is constituted in such a way. But the most remarkable feature in cellulose, starch, and glycogen is the absence of any sugar residue possessing the structure of γ -glucose, and on first inspection, this may be regarded as somewhat damaging to the theory that the reactive type of this sugar plays a part in natural syntheses. On the other hand, a greater importance must hereafter be attached to position 5 in the glucose molecule, as it functions in the coupling of the hexose residues in five highly important saccharides. In submitting these formulae, it is perhaps necessary to sound a note of caution, as the double assumption is made that maltose is an integral part of starch, and similarly that the cellobiose unit is present in cellulose. There seems no reason to doubt these conclusions and they are generally accepted, but they have not been proved.

Issues which are of special interest to the physiologist are raised in the relationship now established between starch and cellulose on the one hand, and between starch and lactose on the other, as one molecular fragment is common to all the compounds. A similar statement may be made regarding sucrose and inulin, as will be evident from the consideration of this polysaccharide.

Inulin.—A common view is that inulin is the direct analogue of starch, from which it differs in being based on fructose in place of glucose. The distinction is, however, more deeply-seated than the above statement implies, and inulin occupies a position which is unique among natural carbohydrates. It is the only compound, so far as known, which is built up of hexose units belonging exclusively to the type known as " γ -sugars." This feature of the polysaccharide has already been referred to, and a diagrammatic scheme will show the succession of reactions which lead to this conclusion.

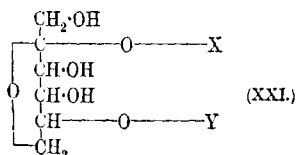


The ultimate products A and B are definitely isomeric, and a fundamental change in structure must therefore take place during one of the reactions involved. On the basis of evidence which, if complicated, is nevertheless conclusive, it has been shown that it is the conversion of inulin into levorotatory fructose which is at fault. During this change the internal ring in the sugar assumes the stable butylene-oxide position. This is not present in the original polysaccharide, but no such intramolecular change from the unstable to the stable type is possible in the parallel hydro-

lysis of trimethyl inulin, as the hydroxyl group necessary for the alteration is substituted.

Our earlier work on inulin established several points of primary importance. All the fructose residues were proved to conform to the γ -type, and, moreover, each C_6 unit was shown to contain three hydroxyl groups. One important piece of structural evidence remained undetermined, but this can now be supplied.

If the hydroxyl groups in inulin are similarly distributed among all the C_6 chains, then the trimethyl γ -fructose obtained from trimethyl inulin must be a single chemical individual. Conversely, in the event of the hydroxyl groups being unsymmetrically arranged, then a mixture of the four possible trimethyl γ -fructoses would result. To obtain the necessary evidence has been difficult, and has demanded the preparation of large quantities of trimethyl γ -fructose which, unfortunately, is a viscous, uncrystallisable syrup. The liquid has been shown to be homogeneous in every respect, and the complete symmetry of the inulin molecule is thus established. It is, on paper, a simple matter to utilise these results so as to construct a molecular formula for inulin, but some doubt still remains as to the constitution of trimethyl γ -fructose. The compound has the same internal oxygen ring which is present in the ketose component of sucrose, but the position of the unsubstituted hydroxyl group is not yet determined with certainty. Until this has been done, it is premature to ascribe a complete structural formula to inulin, but the most probable structure is



the same unit being represented at XY or at X and Y.

γ -Sugars.

In the preceding sections, I have been under the necessity from time to time of referring in passing to γ -sugars, and it seems expedient, in closing, to summarise our knowledge regarding these important variations in sugar molecules. This is desirable, as hitherto no attempt has been made to compile a general survey of what is known regarding γ -sugars and, as considerable interest is taken in these compounds, I begin with the statement that the name applied to them is not descriptive, but is, in a sense, accidental.

As is well-known, the best-defined reducing sugars can generally

be obtained in two isomeric forms which display mutarotation in opposite directions, and this is attributed to the rearrangement of the groups in the reducing position. The expressions α and β were applied to designate these isomerides, and the two mutarotatory forms of glucose serve as standard examples in illustration. Now this isomerism has been proved to be in no way dependent on the position of the internal oxygen ring in the sugar, since both α - and β -glucose have been correlated with the butylene-oxide form of tetramethyl glucose. The discovery that another variety of glucose exists, in which the oxygen ring is differently attached, could not be accommodated by the nomenclature then in use, and the expression " γ -glucose" was applied to it. The name " γ -sugars" has therefore a very general significance, and is used to include all forms in which the oxygen ring is displaced from the normal stable position. This is not entirely satisfactory, but a more exact nomenclature cannot be applied until the complete structure of each of these sugars has been established. Meanwhile it may prevent confusion if it is pointed out that γ -sugars, retaining as they do a reducing group, can exist in α - and β -modifications, and the same remark applies to their glucosides.

Up to the present, it has been ascertained that glucose, galactose, mannose, rhamnose, and fructose are all capable of existing in γ -forms, and there seems no reason to doubt that the property is general. In no case, however, has an unsubstituted γ -sugar been isolated, although we recognise their transient existence, and can in some measure study their properties by examining their methylated derivatives. The presence of the methyl groups in these derivatives prevents any alteration in the oxygen ring, and thus the constitutional type is preserved. Before summarising the chemistry of γ -sugars, it may be mentioned that their discovery did not originate in any single dramatic observation, but that the evidence accumulated gradually. One of my laboratory notebooks, describing work carried out exactly twenty years ago, gives an account of the methylation of sucrose, and the separation of the sugars thereafter formed on hydrolysis. Crystalline tetramethyl glucose was isolated and, in addition, the corresponding fructose derivative was obtained by means of condensation in the cold with methyl alcohol, followed by the usual fractional distillation and hydrolysis. The complete analysis of the product was carried out, its composition was ascertained to be that of a tetramethyl fructose, and its specific rotation was shown to be of the order $+27^\circ$. The entry in the book states that the work was at this stage suspended, there being no adequate explanation as to why a methylated fructose should be dextrorotatory. The

compound was, in fact, pure tetramethyl γ -fructose, but many consecutive researches were necessary before the discovery could be interpreted. A subsequent paper on the methylation of fructose added materially to the evidence that the ketose can react in a dextrorotatory form, and about the same time a result of equal significance was forthcoming. A lævorotatory trimethyl glucose was obtained from glucose monoacetone and, in investigating the origin of this compound a new lævorotatory form of tetramethyl methylglucoside was isolated, *thus showing that, not only can d-fructose react in a dextro-form, but d-glucose can exist in a lævorotatory variety.*

At this stage, Fischer published his paper on γ -methylglucoside, which was quickly followed by our account of the isolation and properties of tetramethyl γ -glucose. In view of this theoretical development, the way was now clear to resume the study of sucrose and to expand the scope of our work.

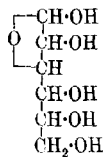
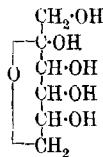
For reasons already stated, the properties of γ -sugars have to be inferred from those of their methylated derivatives, and, so far, the following examples together with the corresponding "methylglucosides" are available for study :

Tetramethyl γ -glucose (lævo)
Trimethyl γ -glucose (lævo)
Tetramethyl γ -galactose (lævo)
Tetramethyl γ -mannose (lævo)
Tetramethyl γ -fructose (dextro)
Trimethyl γ -fructose (dextro)

In reviewing the reactions of these sugars, one is struck by the close resemblance shown to natural processes. For example, the compounds undergo oxidation with extreme ease, being affected by mild oxidising agents, and in illustration it may be mentioned that trimethyl γ -glucose reduces Fehling's solution instantaneously in the cold. At the ordinary temperature also they are converted into glucosides at a speed which is remarkable, especially when it is remembered that the formation of α -methylglucoside requires a treatment of approximately sixty hours at 100°. In at least one case (tetramethyl γ -galactose) a reducing sugar of the γ -type is known to pass spontaneously by auto-condensation into a non-reducing disaccharide. These striking properties are far removed from those of a normal sugar.

Great difficulties have been encountered in attempts to solve the constitution of γ -sugars, and experimental work has been largely confined to tetramethyl γ -glucose, trimethyl γ -fructose, and tetramethyl γ -fructose. In the case of the glucose derivative, the

first opinion formed was that an ethylene-oxide ring was present, but this view has been modified in favour of the propylene-oxide structure. Similarly, an anylene-oxide constitution is at present supported for tetramethyl γ -fructose, so that, meanwhile, the parent sugars may be represented as

 γ -Glucose. γ -Fructose.

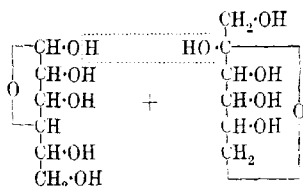
It is already evident that the butylene-oxide structure cannot be assumed for any sugar even in its most stable form. Thus crystalline xylose, which displays none of the properties of a γ -sugar, has recently been shown to be an anylene-oxide and in this respect at least resembles γ -fructose.

I admit that speculation in the absence of experiment is best avoided in the carbohydrates, but in the course of investigating many varieties of γ -compounds I found it impossible to reject the idea that the ordinary crystalline, comparatively stable sugars of the laboratory are not the forms which are primarily elaborated by the plant or disrupted by the animal. The fructose which we store in the chemical museum and produce as a lecture specimen is not fructose as it exists in combination in sucrose or in inulin.

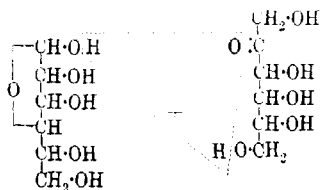
The idea conveyed above is that the natural processes leading to the formation of sugars and their derivatives, as also the ultimate utilisation of carbohydrates by the animal organism, involve as intermediate stages the transient formation of γ -forms. The evidence may not be particularly convincing save to those who have handled all types of carbohydrates at the working bench, but it is certainly the case that we have fleeting glimpses of extraordinarily reactive sugars, which, in the process of artificial isolation from either plant or animal sources, undergo rearrangement to the sugars as we know them. This is not inconsistent with the results obtained in either hydrolysis or synthesis effected by enzymes. If this suggestion is substantiated, it may have far-reaching effects in studying physiological processes, and in the treatment of conditions such as diabetes, in which the metabolism of sugars is abnormal. Research designed to test this idea was commenced three years ago, and the first tentative steps have been taken to ascertain if living tissue promotes the formation of γ -glucose. The evidence obtained is encouraging, but further progress is hampered

by the inaccessibility of γ -sugars and the lack of trustworthy methods of identifying them. When it is remembered that γ -glucose and γ -fructose revert instantaneously to their respective stable forms in the presence of 0.1 per cent. of hydrochloric acid, it will be agreed that there is little prospect of detecting these fugitive isomerides by ordinary processes. Analytical methods are of no avail, and polarimetric evidence alone is insufficient and often misleading. No doubt these difficulties will be surmounted in time, but only when the detailed chemistry of γ -sugars has been advanced on systematic lines, and when knowledge exceeds impatience.

Having in a sense created γ -sugars for you, it may appear contradictory if I say that I have some doubts as to whether these substances are, after all, chemical individuals. They may only represent a condition of the sugar molecule which originates in the mechanism whereby a sugar forms certain of its derivatives. To make the point clear by means of an example, we need not assume that in the formation of sucrose a molecule of normal glucose condenses with a molecule of γ -fructose in such a manner that each loses a hydroxyl group.



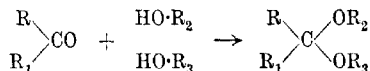
I suggest that γ -fructose may have no real existence, and that the condensation may be equally well explained on the assumption that fructose functions as a ketone. In such a case, two hydroxyl groups become involved, and although one of these must be the reducing group of the aldose molecule, there is no reason, once the reaction is initiated, why the ketose itself should not furnish the second group.



An amylene-oxide ring is thus formed in the ketose component, and here we see *the production of a γ -residue without the previous existence of a γ -sugar*. Similar considerations apply to the formation of γ -glucose derivatives which may be formed in condensation reactions in which glucose reacts as an aldehyde. These suggestions are not without the support afforded by numerous analyses, and meanwhile the whole subject is a maze of possibilities, and enlightenment is still remote.

For example, if the question is raised as to why sucrose is so remarkably unstable towards hydrolysts, the existence of an amylene-oxide ring in the fructose component provides no answer. Methylxyloside is likewise an amylene-oxide, yet the compound resists the effect of dilute acids, whilst β -glucosan, which contains a hexylene-oxide ring, is notably stable. Again, fructosemono- and diacetones both undergo hydrolysis with a facility which resembles that displayed by sucrose, but nevertheless both of these compounds are based on the stable type of fructose in which a butylene-oxide ring is present. These apparently contradictory results reveal that the special instability of γ -derivatives does not depend primarily on the presence of any particular internal ring in the sugar.

On the other hand, when aldehydes or ketones condense with hydroxy-compounds (including sugars), the products resemble sucrose in their ease of hydrolysis. Numerous isopropylidene and benzylidene derivatives may be quoted in illustration and the reactions in which such compounds are formed have been shown to follow the course indicated below:



Applying this to the special case of carbohydrates, γ -sugars may be regarded in a new light. γ -Fructose may, in fact, be nothing more than the ketonic form of the sugar, and γ -glucose the corresponding aldehyde. It may well be that the aldoses and ketoses, functioning in their primary capacity as aldehyde and ketone, are the reactive sugars in nature, but this much seems clear. No naturally-occurring compound of glucose, whether glucoside, disaccharide, or polysaccharide, has been found to contain the γ -glucose structure and the reactive type of the sugar has hitherto been obtained only under artificial conditions. In sharp contrast, the two most important natural derivatives of fructose are each based on γ -fructose, which may possibly prove to be the connecting link in natural processes whereby the interconversion of ketoses and aldoses is effected.

The structural studies which I have laid before you are admittedly incomplete and the various formulae now suggested represent only stages in knowledge and have no claim to finality. Much reliance has been placed on the validity of the methylation process as a means of determining constitution, but it has to be remembered that in the carbohydrates most speculation of the kind is now based on results obtained by this particular method. If I may add one personal note, it is that I have submitted these results, not as an individual contribution, but as the work of a loyal research school. The colleagues, collaborators, and students who have played their part in the laborious work involved, if unnamed now, are always gratefully remembered by me. But one name may be mentioned, for memory dwells specially on the one who carried the spirit of this Society to St. Andrews and who provided the facilities and the enthusiasm which it has been my good fortune to share. I refer to Thomas Purdie.

ANNUAL GENERAL MEETING,

THURSDAY, MARCH 22ND, 1923, AT 4 P.M.

SIR JAMES WALKER, D.Sc., F.R.S., President, in the Chair.

A statement was made by the Treasurer regarding the finances of the Society for the past year, and the adoption of the Report of Council, together with the Balance Sheet and Statement of Accounts for the year ending 31st December, 1922, proposed by Col. C. T. Heycock and seconded by Prof. J. B. Cohen, was carried unanimously.

REPORT OF COUNCIL, 1922-1923.

THOUGH the past year shows a considerable diminution in the number of new Fellows elected, 238 as compared with 349 in 1921, the Council is gratified to report that the Society continues to increase in membership.

On December 31st, 1921, the number of Fellows was 3,912. During 1922, 238 Fellows were elected and 11 reinstated, making a gross total of 4,161. The Council regrets that the number of Fellows who have resigned or allowed their membership to lapse owing to non-payment of annual subscriptions is unusually heavy in the year under review, no less than 63 resignations having been received and 88 Fellows removed, as against the corresponding figures of 49 and 54 in 1921. Thirty-seven Fellows have died, and election has been declared void in the case of 6 newly elected Fellows. The total number of Fellows as at 31st December, 1922, therefore, was 3,967, showing an increase of 55 over that of the previous year.

The sincere congratulations of the Society are offered to Mr. William Spiller, elected on January 15th, 1863, who has been a Fellow for more than sixty years, and to the following who have attained their jubilee as Fellows:

	Elected.
Edmund Neville Nevill	June 1st, 1871.
Joseph Arderne Ormerod	May 16th, 1872.
Archibald Liversidge	Nov. 7th, 1872.
Joseph Leinson Wills	Dec. 5th, 1872.
Thomas Williams	Dec. 5th, 1872.
Sir George Thomas Beilby	Dec. 19th, 1872.
George Brownen	Feb. 20th, 1873.

It was with the greatest regret that the Council accepted, in October last, Dr. M. O. Forster's resignation of the office of Treasurer. Since 1901, with but two years' break, Dr. Forster

rendered the Society most willing and valuable service in the capacities successively of Member of Council, Secretary, Vice-President, and Treasurer. In accepting Dr. Forster's resignation, the Council expressed its most cordial appreciation of his services and its good wishes for his success in the important work he had undertaken.

Prof. J. F. Thorpe was selected by the Council to fill the Treasurership until the next Annual General Meeting, while the vacancy thus created in the Vice-Presidents was filled by the appointment of Dr. J. T. Hewitt for the same period.

The Council received with deep regret the news of the death of Prof. Alexander Crum Brown, who held the office of President from 1891—1893, and who had been a Fellow of the Society for more than fifty-six years. Sir James Walker has undertaken to prepare an obituary notice for the Transactions.

The Society has to mourn the loss of two of its distinguished Honorary Fellows, Prof. Ph. A. Guye, who died on March 27th, 1922, and Prof. Georg Lunge, whose death took place on January 3rd, 1923. Six Honorary Fellows have been elected, so that the present number is 28.

The volume of Transactions for 1922 contains 2,919 pages, of which 2,806 pages are occupied by 347 memoirs, the remaining 113 pages being devoted to Obituary Notices, the War Memorial, the Trust Deed of the Edward Frank Harrison Memorial Trust, lectures on special subjects, the Report of the General Meeting, and the Presidential Address. The volume of the preceding year contained 243 memoirs, occupying 1,990 pages. The Journal for 1922 contains also 5,453 abstracts, occupying 2,116 pages, whilst the abstracts for 1921 numbered 4,005, and occupied 1,636 pages. This very large increase in the number of abstracts over the preceding year is not entirely due to the increased number of papers on chemistry published during the year; as stated in the last Report, owing to delay in transmission of foreign journals in 1921, a considerable number of abstracts (probably between three and four hundred) which should have appeared in that year are published in the present volume.

The abstracts may be classified as follows:

PART I.					Pages.	No. of Abstracts.
Organic Chemistry	—	1937
Physiological Chemistry	—	623
Chemistry of Vegetable Physiology and Agriculture					—	417
					1228	2977

PART II.

General and Physical Chemistry	—	1179
Inorganic Chemistry	—	493
Mineralogical Chemistry	—	73
Analytical Chemistry	—	731
				888	2476
Totals in Parts I and II	2116	5453

The number of reprints supplied free by the Society has been increased from 10 to 25, plus 10 extra for each author of a paper in excess of one.

The Council desires to thank the Abstractors and the Contributors to the Annual Reports for their valuable services during the past year.

It has been decided to publish in the Transactions, when ready, the International Table of Radioactive Elements and their Constants as well as the Table of Isotopes prepared under the auspices of the Union Internationale de la Chimie Pure et Appliquée. Further, in connexion with the Union, a Bureau for Physico-chemical Standards has been established at Brussels University; this Bureau will serve as a centre for the preparation and collection of substances of the highest purity, the physical constants of which have been determined with precision and which shall be at the disposal of research workers.

The Memorial to Lieut.-Col. E. F. Harrison and other Fellows of the Society who fell during the War, has now been erected, and was unveiled on the 15th November last by the Rt. Hon. the Earl of Crawford and Balcarres, K.T. The artistic merit of the combined Memorial is admitted by all, and the Council desires to associate itself most cordially with the tribute paid by Lord Crawford to the work of the artist, Mr. Ernest G. Gillick. The alterations incidental to the erection of the Memorial have resulted in a very notable improvement on the landing outside the meeting room, and the appreciative thanks of the Council have been conveyed to His Majesty's Office of Works for the generous assistance afforded in this matter.

The Harrison Memorial Committee has handed over the balance of their funds in trust to the Chemical Society for the foundation of a prize to be awarded every three years for outstanding original work by young chemists. The terms of the Trust Deed have been published as a part of the Transactions for 1922.

As is well known, the Society of Chemical Industry has recently begun the publication of a weekly journal entitled "Chemistry and

Industry." It appeared to the Council that such a journal might prove a valuable factor in consolidating the interests and strengthening the influence of the various chemical and allied Societies in this country. On this ground and in its desire to support the project, the Council undertook to send copies of the first six issues to all those Fellows who are not Members of the Society of Chemical Industry, and to distribute the new journal throughout 1923 to those Fellows (not being Members of the Society of Chemical Industry) who expressed a desire to receive it. The copies required for this purpose (exceeding 500) are being supplied free by the Society of Chemical Industry, the charge of 10s. per Fellow being made to cover postal and other expenses.

During the past year a scheme for co-operation with the American Chemical Society in the future conduct of the Journal of Physical Chemistry has been inaugurated. According to this scheme the Journal from January 1924 onwards will be issued under the joint auspices of the American Chemical Society, the Chemical Society, and the Faraday Society. The control will be in the hands of an Editorial Board, consisting of four American members and four British members (three appointed by the Chemical Society and one by the Faraday Society) together with an Editor-in-Chief, chosen by these eight members. The Chemical Society representatives on the Board are to be Prof. T. M. Lowry, Prof. J. W. McBain, and Prof. J. C. Philip. The Faraday Society is represented by Prof. F. G. Donnan, whilst the American members are Dr. Arthur L. Day, Prof. G. A. Hulett, Dr. Irving Langmuir, and Dr. W. Lash Miller. These eight members of the Editorial Board have already appointed Dr. Wilder D. Bancroft as the first Editor-in-Chief.

The warm thanks of the Council were accorded to Sir William A. Tilden for the gift of a letter from Sir Humphry Davy and a photograph of the late Lord Rayleigh; to Mr. G. H. Gabb for a copy of the Priestley Medal, and to the Maccabæans for a replica of the Meldola Medal.

The Council arranged for four lectures to be given during the Session 1922—1923. The first was held on October 26th, when Sir William Bragg delivered his lecture on "The Significance of Crystal Structure"; Prof. C. H. Desch gave his lecture entitled "The Metallurgical Applications of Physical Chemistry" on December 14th, whilst on February 22nd Principal J. C. Irvine delivered his lecture on "Some Constitutional Problems of Carbohydrate Chemistry." The Baeyer Memorial Lecture, by Prof. W. H. Perkin, will be given on May 10th, and on June 14th Prof. C. Moureu will deliver (in French) a lecture entitled "Les Gaz

Rares des Sources Thermales, des Grisous et autres Gaz Naturels." Such special lectures continue to meet with keen appreciation, and the Council desires to record its great indebtedness to those gentlemen who so generously place their services at the disposal of the Society.

Facilities have again been granted to London County Council teachers to attend the Ordinary Scientific Meetings. This privilege does not apply to attendance at the Lectures.

The Council has nominated Sir William J. Pope to represent the Society on the Council of Honour of the International Air Congress to be held in June, 1923.

An address of congratulation to the University of Padua on the celebration of the 700th Anniversary of its foundation was presented to the University by Mr. A. Chaston Chapman, who, together with Prof. G. Barger, represented the Society on the occasion.

At the celebration of the 150th Anniversary of the foundation of the Académie Royale de Belgique, Sir William J. Pope represented the Chemical Society.

Prof. H. E. Armstrong and Mr. E. V. Evans were appointed to represent the Society on the deputation to the Minister of Health organised by the Coal Smoke Abatement Society to urge the Government to take immediate steps to deal with smoke abatement and to give legislative effect to the unanimous recommendations of Lord Newton's Departmental Committee.

During 1923 the Society will be represented on the Federal Council of Pure and Applied Chemistry by Prof. J. C. Philip, Sir William J. Pope, and Prof. J. F. Thorpe.

An appeal from the Federal Council for financial support received the sympathetic consideration of the Council. The object in view is to provide a central building in which the chemical societies of the country can be adequately housed. Towards the current expenses of the Federal Council, the sum of £100 has been granted by the Council for 1923. Further, the Society agreed to pay the travelling expenses of two delegates from the Federal Council to the International Conference held at Lyons in June-July, 1922.

After due consideration the Council decided to terminate, as from 31st December, 1922, the Society's membership of the Conjoint Board of Scientific Societies.

At the request of the Association of British Chemical Manufacturers, the Council nominated Dr. J. T. Hewitt and Prof. J. F. Thorpe as the Society's representatives on the Provisional Committee to organise the Chemistry Section of the British Empire Exhibition.

A Committee has been formed at Rome to make arrangements

for the celebration of the 75th birthday of Prof. Emanuele Paternò. It is proposed to found a Paternò Medal to be awarded annually to the chemist, in Italy or elsewhere, who makes the most important discovery of the year. Subscriptions may be sent to the Treasurer of the Chemical Society, Prof. J. F. Thorpe.

In view of the continued distress in Russia, the President issued in September last a further Appeal on behalf of Russian Men of Science and the gratifying sum of more than £210 has at present been received, besides many valuable parcels of clothing and books. Some £115 has been spent since September last on the purchase of clothing and food, and it is satisfactory to report that up to the present every parcel, whether of food, clothing, or books has reached its destination.

In reply to the Committee of Intellectual Co-operation of the League of Nations, attention was drawn to the decision of the Council to send the Journal for 1922 to those Universities and Technical High Schools in Austria which made application. So far the University of Vienna is the only institution which has applied.

In response to an appeal from the Institute of Physics for support of the guarantee fund for the proposed Journal of Scientific Instruments, the Council has agreed to contribute the sum of £50 to the fund.

The Council has also decided to subscribe £100 annually for three years towards the expenses incurred in the publication of the Annual Tables of Constants and Numerical Data.

The attention of the Council has been drawn during the past year to advertisements in the chemical Press in which the names of Fellows appeared followed by the letters "F.C.S." The Council deprecates the use of these letters by Fellows in such connexion, since the letters do not denote a professional qualification.

As announced in the last Report of Council, an arrangement is in force by which Fellows of the Chemical Society are afforded facilities for reading papers on pure chemistry before meetings of the Provincial Local Sections of the Society of Chemical Industry, and the Council is gratified to record that advantage has been taken of this arrangement at a number of centres.

The attention of the Council having been directed to the decision of the Government to discontinue scientific inquiry into questions of indigo production in India, a memorial was presented to the Secretary of State for India strongly deprecating this step, which was viewed with the utmost concern by those interested in the industry in India and in the future of the textile trade of this country. The India Office informed the Council that the memorial had been brought to the notice of the Indian Government.

Following the reports of the Committee on the standardisation of scientific glassware, the Director of the National Physical Laboratory invited the Chemical Society to contribute to the expenses of further proposed work on these lines. The Council, however, declined to do this on the ground that the financial responsibility for such investigations would most appropriately be undertaken by the Scientific and Industrial Research Department.

The additional advantages afforded by the extension of the Library and the increased hours of opening continue to meet with appreciation. Excluding the evenings on which meetings of the Chemical Society were held, there were 5,719 attendances during the past year as compared with 5,434 in 1921. Of the 5,719, 4,229 were made by our own Fellows, while 1,490 were made by members of contributing Societies, as against 1,195 in 1921.

A comparison of the number of books borrowed from the Library during 1922 with that for 1921 gives the figure 4,145 as against 3,585. Since 1919, the year in which the full scheme was first in operation, the proportion issued to persons other than Fellows of the Chemical Society has been 11.1 per cent. (1919), 15.7 per cent. (1920), 18.8 per cent. (1921), and 20.9 per cent. (1922); whilst as regards attendances the corresponding figures are 15.4 per cent., 15.8 per cent., 22.0 per cent., and 26.1 per cent.

The additions to the Library comprise 216 books, of which 93 were presented, 690 volumes of periodicals (including a gift of 164 volumes from the Society of Chemical Industry), and 39 pamphlets, as compared with 244 books, 441 volumes of periodicals, and 168 pamphlets last year.

The total amount expended on the Library in 1922 was approximately £1,572 10s., towards which the sum of £421 10s. was received from contributing Societies. There is reason to think that the expenses of the Library will continue to increase and the Council earnestly hopes that the contributing Societies will give the scheme their generous support.

The Library now contains 26,738 volumes, consisting of 8,029 books and 18,709 bound volumes of periodicals.

In response to a request from the Institute of Chemistry, registered Students of the Institute have been allowed during the year the use of the Library for reading, but not for borrowing, purposes.

The accounts of the Society for the past year give an excess of expenditure over income of £136 10s. 1d., the total income being £140 4s. 8d. less than in 1921. On comparing the accounts of the two years it will be seen that the amount received for Life Composition Fees in 1922 is £1137 10s. less than in 1921, and the interest

from deposit is £44 13s. 1d. as against £88 12s., whilst the net income from advertisements shows a diminution of £31 5s. 1d. Against these, the Annual Subscriptions show an increase of £250 12s., and the sales of publications have realised £958 19s. 3d. more than in 1921. Had the Life Composition Fees equalled those received in 1921, the total income would have shown an increase of £997 5s. 4d. On the recommendation of the Finance Committee, the Council has decided in future that the amount received as Life Composition Fees shall be capitalised, only the interest accruing therefrom appearing in the Income and Expenditure Account.

Apart from the War Memorial, which cost £451 10s. 2d., the total expenditure in 1922 exceeds that for 1921 by £25 18s. 7d. The principal items showing an increase are Abstractors' Fees, £221 16s. 2d.; Distribution, £213 19s., and Authors' Copies, £96 0s. 2d. The cost of printing the Journal, which occupies 5035 pages and is 1264 pages longer than in 1921, has risen by £122 5s. 7d. only, as against £1442 19s., the corresponding figure in last year's accounts when the Journal showed an increase of 415 pages over that for 1920. The previous highest number of pages in the Journal was 4977 in 1914. On the other hand, owing to a substantial reduction in the charges for paper and binding, the Annual Reports for 1921 cost £205 5s. 5d. less than the preceding volume, and the List of Fellows shows a saving of £32 5s. 4d.

In the last Report the hope was expressed that the cost of the Journal per page had reached its maximum, and it is gratifying to record a substantial reduction this year, the cost being £2 0s. 6d. per page as against £2 12s. 4d. in 1921. During the past twelve months, paper has fallen in price, whilst in the latter part of the year there have been two cuts in printing charges amounting to nearly 10 per cent.; there should thus be a still further diminution in the cost per page of the Journal in 1923, since these reductions will apply to the whole year.

The value of the Society's Securities now stands at £36,475 6s. 3d., showing an increase of £3468 17s. 7d. over that of the previous year.

On the advice of the Bankers, the Council decided to sell the Metropolitan $3\frac{1}{2}$ per cent. stock, of which £6730 was held on General Account and £4400 on the Research Fund Account, and to devote the proceeds to the purchase of $3\frac{1}{2}$ per cent. Government Conversion Loan, 1961. The Metropolitan Stock was sold at $92\frac{1}{2}$ ex dividend and the new stock purchased at 75 $\frac{1}{2}$. The Society now holds £8272 10s. 3d. Conversion Loan on General Account and £5408 1s. 1d. on Research Fund Account. Allowance being

made for the fact that a full half-year's interest becomes payable on 1st April, 1923, this will provide an increase of annual income of nearly one per cent. It has also been decided to sell the £4300 National War Bonds, of which £4000 is on General Account and £300 on Research Fund Account, and to devote the proceeds to the purchase of $3\frac{1}{2}$ per cent. Government Conversion Loan.

The Council has had under consideration the question of the Society acting as its own publishers, but after deliberation it was agreed to accept the offer of Messrs. Gurney & Jackson to continue to act as publishers on a total commission of all sales amounting to 10 per cent.

Arrangements for the publication of Volume VI of the Collective Index (1913-1922) are well in hand, and it is hoped to publish the Authors' Index in May or June, 1923, the Subject Index following in March 1924. The price of the Index was fixed at £2 17s. to Fellows applying by Christmas, 1922, and at £3 7s. to those making application thereafter. A considerable reduction has been made in the prices of Volumes I to V of the Collective Index, as stated on the slip attached to the Journal for January, 1923.

The Society's Fire Insurance has been increased and now covers the War Memorial. A policy has also been taken out insuring the books in the basement against damage caused by water.

A Committee was appointed to consider whether it would be advisable to place in the hands of an agent the arrangements connected with the advertisements appearing in the Journal, and the Council adopted the report of the Committee advising that the matter should continue to be left in the hands of the Assistant Secretary.

The Grants from the Research Fund amount to £836 7s. 6d. as against £629 in 1921, and exceed the annual assured income by some £240. The following Research Grants were made during the year, the Council making a recommendation to the grantees that the materials required for the research for which the grant was made should, as far as possible, be purchased in this country :—

	£	s.	d.
Hydrogen ion concentration for hydroxides, carbonates, and sulphates of some of the rarer elements. W. R. G. Atkins	10	0	0
Condensation of ketones. A. J. Attwood	12	0	0
Action of bromine in the presence of pyridine on compounds of the benzene and naphthalene series. E. de B. Barnett	5	0	0
Studies in the anthracene series (continued). E. de B. Barnett	10	0	0
Study of certain fused reciprocal salt-pair systems. H. Bassett.	2	7	6
The study of some aliphatic and cyclic sulphides. G. M. Bennett	10	0	0
Researches on reaction velocity. E. J. Bowen	10	0	0
Experiments on gels and on the theory of solutions. S. C. Bradford	10	0	0

	£	s.	d.
Experiments on the decomposition of tungsten and other metals. H. V. A. Briscoe	50	0	0
Physico-chemical researches on some of the rarer metals and their salts. H. T. S. Britton	5	0	0
The effect of electro-negative substituents on the carbon tetra- hedral angle. C. C. M. Broughton	12	0	0
Action of fuming sulphuric acid and allied reagents on saturated aliphatic and alicyclic hydrocarbons and some derivatives (continued). G. N. Burkhardt	10	0	0
The mechanism of the inhibition of indole-production by indole- producing bacteria. B. H. E. Cadness	10	0	0
Studies in ring formation (continued). W. A. P. Challenor ...	20	0	0
Interaction of sodium chloride and various oxides at elevated temperatures. F. H. Clews	10	0	0
Aliphatic sulphonamides (continued). J. B. Cohen	5	0	0
The Friedel-Crafts' reaction. Anomalies and modifications. M. Copisarow	10	0	0
Kinetics of the reaction between sodium alkyl acetoacetic esters and alkyl iodides. J. J. Creasy	10	0	0
(a) Synthesis of certain polynuclear nitrogenous ring systems ...	10	0	0
(b) Steric hindrance and substitution in the aromatic series. W. Davies			
Formation of <i>gem</i> -disubstituted tetrahydropyrrole rings. F. Dickens	15	0	0
Electrolytic precipitation of certain hydrosols. J. J. Doonan ...	7	0	0
Resolution of <i>dl</i> -apomorphine. W. Doran	10	0	0
Interaction of PhN_3 and menthyl cyanoacetate and related reactions. P. K. Dutt	10	0	0
Preparation of derivatives of mercury dibenzyl and of analogous compounds. P. Edgerton	15	0	0
The alkylation and ring-chain tautomerism of the dihydro- resorcinyl esters. W. E. Ellis	10	0	0
Electro-osmosis. F. Fairbrother	12	0	0
Unsaturated cyclic ketones and their employment in the pro- duction of associated ring systems. E. H. Farmer ...	12	0	0
The sorption of gases by carbon. J. B. Firth	10	0	0
The effect of an accumulation of alkyl groups on the ease of forma- tion of the cyclopropane ring in glutaric acids. P. M. Fisk	12	0	0
The temperature coefficient of the reaction velocity in the action between methyl iodide and various alkyl oxides of sodium. W. J. Gale	5	0	0
Absorption spectra of some disulphides and derivatives. D. T. Gibson	3	0	0
Organo-derivatives of thallium (continued). A. E. Goddard ...	5	0	0
Organo-derivatives of antimony. A. E. Goddard	5	0	0
Synthesis of new associated alicyclic systems. F. R. Goss ...	15	0	0
Absorption spectra of organic compounds. H. Graham ...	5	0	0
Mobility of symmetrical triad systems. J. P. Griffiths ...	12	0	0
Chemistry of bridged ring compounds exhibiting intra-annular tautomerism (continued). R. C. Grimwood	15	0	0
Electrochemistry and thermochemistry of solutions of electro- lytes in methyl alcohol. H. B. Hartley	20	0	0

	£	s.	d.
Influence of molecular collisions on the chemical activation of molecules in thermal reactions. C. N. Hinshelwood ...	15	0	0
The reactions of glutaconic acid and its ester. R. T. Holden ...	12	0	0
Synthesis of norpinic acids. C. Hollins ...	10	0	0
New syntheses of diketopyrrolines and of 4-oxazolones. C. Hollins ...	5	0	0
A study of diphasic systems from the point of view of surface tension. S. S. Joshi ...	6	0	0
Influence of the nitro-group on the reactivity of substituents in the benzene nucleus (continued). J. Kenner ...	10	0	0
Resolution of substituted diphenic acids into optically active components. J. Kenner ...	10	0	0
Reactions of β -phenylglutaric acid and its derivatives. J. Kenner ...	10	0	0
Study of bridged-ring compounds (continued). E. W. Lanfear ...	15	0	0
Researches on colloids (continued). J. W. McBain ...	20	0	0
Condensation of α -alkyloxy-ketones. T. Malkin ...	10	0	0
Reactions of a periodic or oscillatory character. J. E. Myers ...	12	0	0
The formation and properties of dithio-ketones and dithio-ethers. K. G. Naik ...	15	0	0
Synthesis of polyacetic acids of methane. L. C. Nickolls ...	10	0	0
Investigation of gallotannin (continued). M. Nierenstein ...	10	0	0
Quantitative determinations of the velocity of splitting of heterocyclic compounds and the effect of size and substituents on the velocity constants. J. H. Oliver ...	12	0	0
Action of liquid nitrogen tetroxide on water at low temperatures. J. R. Park ...	5	0	0
(a) Investigation of the gases evolved from older rocks... (b) The relative affinity for bases of different acids at high temperatures and its bearing on refractory materials. W. H. Patterson ...	20	0	0
Reactions occurring when mixtures of oxygen and ammonia are sparked and the decomposition of ammonia by sparking with electrolytic gas. A. J. Prince ...	13	0	0
The electrical conductivity of aqueous solutions, especially the alkalis and mineral acids. H. R. Raikes ...	12	0	0
Preparation of camphor derivatives containing enlarged rings. L. R. Ridgway ...	10	0	0
Interaction between aldehydes and ketones and aliphatic nitro-compounds. H. A. Scarborough ...	10	0	0
Studies in ring structure. E. A. Seeley ...	10	0	0
The value of the ratio C_p/C_v for gases, particularly nitrous oxide. W. G. Shilling ...	10	0	0
Attempt to prepare open-chain unsaturated compounds which will be tautomeric with their ring isomerides. B. Singh ...	10	0	0
Influence of steric factors on the relative orienting powers of alkyloxy-groups. J. C. Smith ...	10	0	0
The formation of tetrahydronaphthalene derivatives from γ -phenylbutyric acids. A. Stevenson ...	15	0	0
Researches on the surface tension of organic substances. S. Sugden ...	10	0	0

	£	s.	d.
The variation in the degree of hydrolysis with dilution of certain oximo hydrochlorides. L. B. Tansley	10	0	0
Kinetics of successive reactions, with special reference to oxidation and reduction reactions. R. W. M. Thomson	20	0	0
Preparation of methylphthalic acids. H. Toms	10	0	0
Organic compounds of arsenic. E. E. Turner	15	0	0
Formation of four-membered ring compounds by the additive union of two substances each having a double linkage.			
S. D. Weaver	10	0	0
The quantitative reduction by hydriodic acid of halogenated 1:3 diketones and allied substances. R. W. West	15	0	0
Synthesis of diethylthiocarbocyanine iodide. J. B. Whitworth	12	0	0
Absorption of oxides of nitrogen by lime. F. A. Williams	8	0	0
Total	£836	7	6

THE TREASURER then proposed a vote of thanks to the Auditors for their services in auditing the Accounts of the Society for the past year. This was seconded by DR. N. V. SIDGWICK and acknowledged by PROF. T. S. MOORE.

A vote of thanks to the Treasurer, Secretaries, Foreign Secretary, and Council for their services during the past year, proposed by MR. A. CHASTON CHAPMAN, and seconded by DR. J. A. VOELCKER, was carried with acclamation, acknowledgment being made by PROF. H. E. ARMSTRONG, who had served on the Council continuously for a period of fifty years.

THE PRESIDENT declared that the following Fellows, who had been nominated to fill the vacant places on the Council, had been duly elected:

President.—William Palmer Wynne, D.Sc., F.R.S.

Vice-Presidents who have filled the office of President.—Sir William Jackson Pope, K.B.E., M.A., D.Sc., F.R.S.; Sir James Walker, D.Sc., LL.D., F.R.S.

Vice-Presidents who have not filled the office of President.—John Theodore Hewitt, M.A., D.Sc., Ph.D., F.R.S.; Gilbert Thomas Morgan, O.B.E., D.Sc., F.R.S.; John Millar Thomson, LL.D., F.R.S.

Treasurer.—Jocelyn Field Thorpe, C.B.E., D.Sc., F.R.S.

Ordinary Members of Council.—Edward Frankland Armstrong, D.Sc., Ph.D., F.R.S.; Walter Norman Haworth, D.Sc., Ph.D.; Christopher Kelk Ingold, D.Sc.; Hamilton McCombie, D.S.O., M.C., M.A., D.Sc.; Gordon Wickham Monier-Williams, O.B.E., M.C., M.A., Ph.D.; Joseph Reilly, M.A., D.Sc.

Dr. R. C. Farmer, Prof. T. S. Moore, and Prof. J. F. Spencer were unanimously elected Auditors to audit the Accounts of the Society for the year 1923.

THE PRESIDENT then delivered his address entitled "Symbols and Formulae."

A vote of thanks to the President for his eminent services in the Chair during the past two years, and for his address, coupled with the request that he would allow his address to be printed in the Transactions, was proposed by PROF. J. NORMAN COLLIE, seconded by PROF. H. B. BAKER, and carried with acclamation, acknowledgment being made by the PRESIDENT.

<i>Liabilities.</i>		<i>Assets.</i>	
	£ s. d.		£ s. d.
To Subscriptions received in advance :-		By Investments (value when acquired) :-	
at £1 0 0	514 0 0	£1070 Metropolitan Canal, 24 per cent. Stock A ...	7212 8 6
" Sundry Creditors	2402 18 10	£1070 London and North Western Railway 3 per	1890 12 0
" Research Fund :-		£1290 L.A.C. 3d. Carriage Corporation 3 per cent. Stock	1650 0 0
As per last Account	15,388 2 9	£1400 India 24 per cent. Stock	1816 1 0
<i>Less Excess of Expenditure over Income for Year</i>	<i>294 4 1</i>	£1400 Metropolitan Water Board 3 per cent. Debenture	3272 2 5
<i>Excess of Assets over Liabilities per last Balance Sheet</i>	<i>15,187 18 5</i>	£1380 Midland Railway 24 per cent. Stock	3272 2 5
		£1300 London Corporation 3 per cent. Stock	1143 1 0
<i>Less Excess of Expenditure over Income for Year</i>	<i>136 10 1</i>	£1500 Transvaal 2 1/2 per cent. Guaranteed Stock, 1923-53	1400 13 6
<i>Collective Index :-</i>		£1000 British Railway 3 per cent. Debenture	1033 11 0
Receipts less Expenses to date	27,894 1 8	£700 Canada 24 per cent. Stock, 1920/50	704 8 6
Chemistry and Industry :-		£2100 5 per cent. War Stock, 1920/47	1995 0 0
Receipts to date	1092 11 5	£2000 Registered 5 per cent. National War Bonds, 1927	2000 0 0
		£2000 4 per cent. Funding, 1928, 1929/50	2000 0 0
		(Market Value £22,325 15s.)	
		Sundry Debits :-	
		£1000 Metropolitan Railway (No. 1) 4 per cent.	480 0 0
		Preference Stock	98,932 0 1
		£1000 Metropolitan Consolidated 3 1/2 per cent. Stock	2,240 3 8
		Credit :-	
		£112 16s. 6d. New South Wales 3 per cent. Stock	600 0 0
		£1000 Metropolitan Water Board 3 per cent. Debenture	4,87 18 0
		£1360 Midland Railway 24 per cent. Debenture	1049 13 11
		£200 Victoria 2 per cent. Stock	100 0 0
		£2000 National War Bonds 1928, 3rd Series	1002 16 9
		(Market Value £12,140 11s. 3d.)	1010 6 9
		£200 National War Bonds 1928, 3rd Series	706 6 12
		(Market Value £12,140 11s. 3d.)	300 0 0
		Cash at Bank	14,084 2 5
			253 16 3
			<u>£27,164 18 5</u>

I have examined the above Balance Sheet and accompanying Income and Expenditure Accounts with the Books and Vouchers of the Society, and certify them to be in accordance therewith. I have also verified the Balance at the Bankers and the Investments.

Approved: {
 W. B. KEENE,
 T. S. MOORE.

W. B. KEENE
 Chartered Accountant.

28, QUEEN VICTORIA STREET, E.C. 4.
 February 14th, 1928.

INCOME AND EXPENDITURE ACCOUNT

		<i>Income.</i>			
				<i>£</i>	<i>s. d.</i>
To Life Compositions	448	0 0
" Admission Fees	322	0 0
" Annual Subscriptions		
Received in advance, on account of 1922	558	0 0
" during 1922	8270	12 0
" " " 1921	545	2 0
" " " 1920 and previous years	5	0 0
				9558	14 0
Less amount included in last year's Income, being valuation of Arrears as per last Balance Sheet	630	0 0
				8728	14 0
Add Arrears at date: £823 4s.; Estimated to realise as per Balance Sheet	660	0 0
				9388	14 0
Investments, Dividends on:—					
£6730 Metropolitan Consolidated 3½ per cent. Stock	235	11 0
£1050 London and North Western Railway 5 per cent. Debenture Stock	22	8 10
£1520 14s. 3d. Cardiff Corporation 3 per cent. Stock	33	1 0
£1400 India 2½ per cent. Stock	35	0 0
£2400 Bristol Corporation 2½ per cent. Debenture Stock	45	0 0
£4341 Midland Railway 2½ per cent. Preference Stock	78	0 1
£1200 Leeds Corporation 3 per cent. Stock	26	2 0
£1500 Transvaal 3 per cent. Guaranteed, 1923/28	45	0 0
£1200 North British Railway 3 per cent. Debenture Stock	26	5 11
£700 Canada 5½ per cent., 1930/50	17	15 3
£2100 5 per cent. War Stock	105	0 0
£1700 5 per cent. War Bonds	41	5 0
£2000 5 per cent. National War Bonds, 1927	100	0 0
£2000 5 per cent. National War Bonds, 1928	100	0 0
£2000 Funding Loan, 4 per cent., 1920/30	17	8 0
" Income Tax Recovered	167	2 10
" Interest on Deposit	44	13 1
				1679	13 6
Publication Sales:—					
Journals	3170	10 6
Proceedings	10	12 8
Collective Index	93	6 11
Library Catalogue	0	9 6
Atomic Weight Tables	1	7 10
Jubilee Volumes	0	5 0
Annual Reports on Progress of Chemistry	478	10 4
Memorial Lectures (including Fischer Lectures)	7	13 6
General Abstracts	18	0 0
Berichte und Zentralliste	370	0 0
				4450	16 3
Less Publishers' Commission	300	18 10
				4050	17 3
Proceeds of Advertisements in Journal	797	12 10
Less Commission	55	7 5
				742	5 5
Miscellaneous Receipts	0	7 6
Donations to Library	443	0 0
Subscriptions from other Societies	24	5 0
Balance, being Excess of Expenditure over Income, carried to Balance Sheet	136	10 1
				£17,153	11 1

FOR THE YEAR ENDED 31ST DECEMBER, 1922.

<i>Expenditure.</i>		<i>£</i>	<i>s.</i>	<i>d.</i>	<i>£</i>	<i>s.</i>	<i>d.</i>
By Expenses on account of Journal:—							
Editorial Salaries	...	906	4	0			
Editorial Bonus	...	224	0	0			
Editorial Postages	...	52	4	9			
Abstractors' Fees	...	926	6	2			
Printing of Journal	...	7839	15	6			
Binding	...	117	14	4			
Printing of Advertisements	...	210	15	0			
Addressograph Labels	...	8	0	11			
Distribution of Journal	...	1034	1	5			
Authors' Copies	...	448	1	0			
Insurance of Stock	...	15	4	0			
					11,524	17	10
.. Special Lectures, Hire of Hall, etc., ...					29	1	1
.. Annual Reports on the Progress of Chemistry					667	15	8
.. Purchase of Back Numbers of Journal					65	16	0
.. List of Fellows, Printing, etc.					112	4	9
.. Library Expenses:—							
Salaries	...	693	1	7			
Bonus	...	305	5	2			
Books and Periodicals	...	289	14	3			
Binding	...	72	4	3			
					1572	6	10
.. Donations:—							
Conjoint Board of Scientific Societies	...	5	5	0			
Federal Council	...	169	0	0			
					165	5	0
.. Administration Expenses:—							
Salary of Staff	...	854	13	6			
Bonus	...	349	0	0			
Wages	...	341	16	6			
Bonus	...	114	8	0			
Coal and Lighting	...	120	1	7			
House Expenses and Repairs	...	125	0	6			
Telephone	...	27	13	4			
Furniture	...	10	14	8			
Tax Expenses	...	53	18	5			
Insurances	...	15	19	10			
Accountants' Charges	...	31	10	0			
Commission on Recovery of Income Tax	...	5	7	3			
Miscellaneous Printing and Stationery	...	310	17	10			
Postages	...	211	17	7			
Miscellaneous Expenses	...	58	5	10			
Carriage on Journals to Germany	...	2	17	4			
					2624	13	9
					16792	0	11
War Memorial	...				451	10	2

£17,133 11 1

RESEARCH FUND INCOME AND EXPENDITURE ACCOUNT FOR THE YEAR ENDED 31ST DECEMBER, 1922.

<i>Income.</i>		<i>Expenditure.</i>	
	£ s. d.		£ s. d.
To Dividends on —			
£1000 North British Railway 4 per cent. No. 1 Preference Stock (18 months)	42 9 6	By Grants	830 7 6
£1000 Metropolitan Consolidated 3½ per cent. Stock	154 0 0	„ Commission on Recovery of Income Tax	1 11 3
£1034 Great Western Railway 3½ per cent. Debenture Stock	18 8 4	„ Advertisements	3 1 6
£1112 New South Wales 2 per cent. Debenture Stock	34 5 8	„ Notes on Furnishing and Equipment of Chemical Laboratories	16 1 9
£1122 Metropolitan Water Board 3 per cent. No. 1 Stock	33 13 2	„ Repairs to Balance, etc.	7 8 8
£1365 Midland Railway 3½ per cent. Debenture Stock	24 6 8		
£500 Victoria 3 per cent. Stock	17 10 7		
£408 12s. 6d. 5 per cent. War Loan, 1920/47	224 18 6		
£300 National War Bonds, 1928	15 0 0		
	564 12 0		
„ Income Tax Recovered	31 4 11		
„ Re-payment of Grants	68 9 8		
„ Balance, being Excess of Expenditure over Income, carried to Balance Sheet	290 4 1		
	£864 10 8		£864 10 8

PRESIDENTIAL ADDRESS.

Delivered at the ANNUAL GENERAL MEETING, March 22nd, 1923.

By SIR JAMES WALKER, D.Sc., LL.D., F.R.S.

Symbols and Formulæ.

SYMBOLS are both an aid and an obstacle to thought. Their brevity and simplicity may help us, working according to a fixed system, to perform mental operations which without their aid might be practically impossible. Their generality too may, as in algebra, enable us to solve thousands of problems in one. On the other hand, we sometimes find in science a system of symbols which, at first of great value, may in virtue of its very success so warp our thought or limit our mental outlook as to constitute a real hindrance to scientific progress. And there is always the danger, arising from our familiar and constant use of the symbol, either of forgetting what it properly symbolises, or of confusing the symbol with the thing symbolised.

The function of the symbol is a practical one; in Mach's phrase, it is to effect economy of thought, and it is precisely because mankind at large is so economical of thought that the dangers of symbolism originate. The danger, however, must be faced by the student of chemical science, for without symbols systematic advance is impossible: the symbols are based on a theory and permit the representation of that theory in detail.

If we examine the practical requirement of a satisfactory system of symbols we shall find that the system must be simple in itself and simple to operate. Consider the Roman schoolboy confronted with the problem of multiplying MCMXXIII by CXLIV. The system of notation is not too complicated, but to operate with it is practically impossible. To perform his task he must abandon the symbolism and have recourse to concrete objects—the fingers or an abacus. The Arabic notation, on the other hand, with its consistent valuation by position and the introduction of a symbol for zero, enables us, once we have passed the barriers of the addition and multiplication tables, to perform arithmetical calculations of all kinds with ease and speed. It is simple in itself and simple to operate.

The same requirements are essential to a system of chemical symbols. The first symbols, those for the metals known to the ancients, indicated nothing but their supposed association with

the planets and the gods ruling them. Thus the solar disk stood for gold, the lunar crescent for silver, the mirror of Venus for the Cyprian metal copper, and so on. Towards the end of the eighteenth century we see the beginnings of our present system of elementary symbols. Hassenfratz and Adet (1787) used for the non-metals straight and curved lines which could be combined together (much as in phonetic shorthand) to represent the qualitative composition of compounds. The symbol for a metal was a circle and to distinguish one metal from another the initial of its Latin name was written within the circle—thus $\textcircled{\text{sh}}$ was the symbol for antimony.

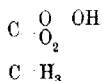
Dalton used for metals and non-metals alike only circular symbols, doubtless to represent spherical atoms, and in his hands the symbols assumed a quantitative significance based upon his atomic theory. For the simple non-metals these symbols were arbitrarily chosen, \bigcirc representing an atom of oxygen, \odot an atom of hydrogen, $\textcircled{\text{N}}$ an atom of nitrogen and so on. For the metals he adopted the same device as Hassenfratz and Adet, using, however, the English instead of the Latin names, so that for example $\textcircled{\text{L}}$ represented an atom of lead. Compounds could be represented by the juxtaposition of the elementary symbols, which now gave, not only the qualitative, but also the quantitative composition of the compound. Thus, for Dalton, water was represented by the symbol $\bigcirc\odot$, denoting the combination of 7 parts of oxygen with 1 of hydrogen. Berzelius (1815) took the final step by using Latin initials for all the elements, dropping the circles which had surrounded them, and employing affixed numerals to indicate the number of times the symbol had to be repeated. It is true that Berzelius spoiled the uniformity of his system by using a special dot symbol for oxygen and writing such formulæ as $\ddot{\text{S}}$ for sulphur trioxide. These dotted symbols, however, found little favour except amongst mineralogists, and gradually passed out of use. The disuse of the circles is not without significance—the symbol to Berzelius represented a combining weight rather than a concrete atom, and the dual quantitative use persists in the interpretation of symbols to-day. The symbol C stands for one atom of carbon or “twelve parts by weight” of carbon. So we may say that more than a hundred years ago a system of formulation had been reached which, with minor alterations, is in use at the present time for the representation of elements and the composition of compounds, and is never likely to be superseded. It is uniform, plain, and simple in itself, and simple to use in the equations representing chemical change.

The purely compositional formulæ, however, fall far short of expressing what calls for expression in various classes of chemical

compounds: action and structure have to be considered as well as composition. The dualistic formulæ of Berzelius illustrate early attempts in this direction. The formula of sodium sulphate is not written empirically as Na_2SO_4 , but dualistically as $\text{Na}_2\text{O}, \text{SO}_3$. This formula indicates *inter alia* that the sodium and the sulphur belong to two essentially different parts of the compound. The modern electro-chemical dualism writes $\text{Na}_2^+\text{SO}_4^-$, again indicating the same division of a positive from a negative portion. In organic chemistry the representation of structure by means of formulæ achieved success by the clear recognition of valency, in particular, the quadrivalence of the carbon atom. At this point of development the notion of the atom as structural unit becomes indispensable.

The valency of an element on its experimental side is in essence a numerical conception. We divide a weight by a weight, namely, the atomic weight by the equivalent weight, and obtain in consequence a mere number. When we pass from element to atom, however, the conception undergoes a transformation, and receives a concrete meaning. The valency of an atom may be interpreted as its capacity for combining with other atoms, again a numerical conception, but one leading directly to a symbolism and indirectly to a mechanical interpretation. Each atom is conceived as having a definite number of places for the attachment of other atoms, and as the number is in each case small, we can conveniently represent it in a graphic symbol.

It is not without interest to look back to the origin of graphic or constitutional formulæ and see the beginnings of our conventional system. Couper and Kekulé, the originators of the idea, suggested systems widely differing from each other. Couper (1858) symbolised acetic acid as follows,



in appearance a near approach to present day usage if we allow for the fact that he assumes $\text{O} = 8$ and $\text{C} = 12$. The manner of linking of various atoms is indicated, but their valency is not clearly symbolised. Kekulé's graphic formula (1859) for the same substance is shown in the figure.

Acetic Acid



(Kekulé.)

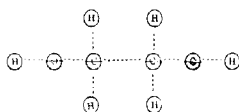


(Loschmidt.)

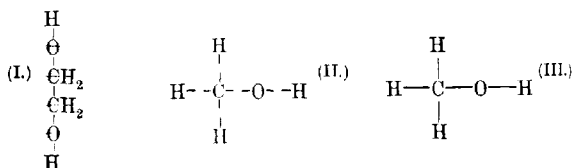
The valency is satisfactorily represented, but the linkage of the atoms is confused. Only atoms touching in a vertical line are supposed to be directly linked. The system is cumbersome, and Kekulé himself used it but sparingly. For branched chains it becomes impracticable.

Loschmidt (1861) devised a clear logical system which, although he formulated by its means hundreds of compounds, some of a very complex nature, found no favour amongst chemists. His symbol for acetic acid is given in the figure. Here linkage and valency are adequately represented but the atomic symbols are arbitrary, and the system, like Kekulé's, is cumbersome to use.

Simultaneously with Loschmidt, Crum Brown (1861), although he was unaware of Couper's work, used a symbolism resembling his, and practically identical with that in current use. He writes glycol as follows :



Here valency and linkage are clear, and the atomic symbols are no longer arbitrary. Wurtz in 1864 gave the following formula (I) for the same substance :

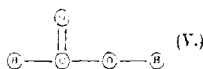
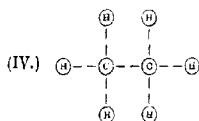


The line of development of modern graphic formulæ then is through Couper, Crum Brown, and Wurtz, and not through Kekulé or Loschmidt. The reason for the preference shown by chemists is that the symbolism adopted is more obvious, simpler to use, simpler to reproduce, and easily adaptable to all organic compounds.

There is a dual character in our graphic formulæ which it is important that we should realise. Let us begin with the graphic symbols of the elements, thus: $\text{H}-$, $-\text{O}-$, $-\text{C}-$, where each short line represents a unit of valency. To the graphic symbols of molecules is but a step; the atoms are represented as united together, the valencies indicating the manner of attachment (II). The directness or indirectness of union of the atoms is here given; no hydrogen atom is in this formula directly attached to another; they are only

indirectly united through carbon or oxygen. For brevity, we join up the lines representing the valencies of the various atoms and obtain the customary formula (III). A great change in significance has, however, at this stage taken place: the valencies have become "bonds"—the idea of force has entered. What that force is remains indeterminate; it is merely something binding atoms together, and the interpretation of the symbols is not quantitative in this respect. The "bonds" do not represent equal forces; it is patent that the bond between hydrogen and carbon in the formula for methyl alcohol represents a different force from that between hydrogen and oxygen. The current symbolism may then be interpreted in two senses; the lines joining the atomic symbols may be taken to represent on the one hand merely the union of the atoms to the symbols of which they are attached, or they may represent forces existing between these atoms. Confusion of these two senses sometimes leads to erroneous reasoning.

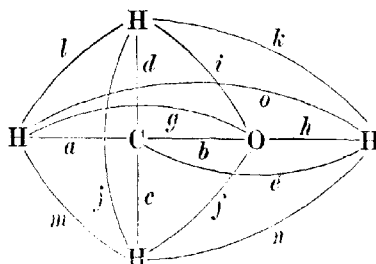
This dual character of graphic formulæ is noticeable from their earliest employment, and I need make no apology in illustrating it from the work of Crum Brown, whose recent death deprived our Society of its senior Past-President. In the formula for glycol quoted above he states (1861) that the dotted lines therein employed represent polar forces. In 1864 he represents ethane thus (IV),



each valence being written independently. He says: "I may here shortly explain the graphic notation which I employ to express constitutional formulæ. . . . An atom is represented by its usual symbol surrounded by a circle with as many lines proceeding from it as the atom contains equivalents. . . . When equivalents mutually saturate one another the two lines representing the equivalents are made continuations of one another." Here he has discarded the idea of polar force in his original formulation in favour of the simpler conception of number of equivalents. In 1866 he writes continuous lines between the symbols, and in 1868 puts the matter thus, "The structural formula of formic acid [V] indicates first, that the four carbon equivalents form one atom, the four oxygen equivalents two atoms, and the two hydrogen equivalents two atoms; secondly, that these equivalents are united in pairs, thus—*co, co, co, ch, ho*, but it does not in any way indicate (and we do not know) what is the *potential* of each of these pairs—that is, how

much energy would be required to separate the equivalents from each other. We know that this potential depends upon the structure, and we can to a certain extent trace the nature of this dependence, but as yet we cannot express the potential numerically, and till we can do that we do not fully know the constitution."

On the one hand, then, our "bonds" stand for mere units of valency, on the other they are an imperfect representation of forces. Were the representation of forces more complete, methyl alcohol would appear somewhat as shown in the figure, the small letters representing numerical values. Even this formula, however, only gives the magnitude and not the real direction of the forces, and is besides static, not kinetic. We naturally shrink from complexity such as this: imagine the formula of sucrose on a similar basis. We must content ourselves with something simpler,

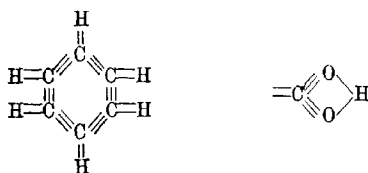


Methyl Alcohol.

and yet the simple valency formula has for long been felt to be inadequate. Apart from the idea of definitely directed valencies which leads to stereochemical formulæ, the idea of representing partial valencies has been constantly in the foreground. We cannot properly split valencies in the old sense, but we can subdivide forces *ad libitum*. If the subdivision is carried too far, however, the formulæ may approach in complexity formulæ with quantitatively measured forces, such as that indicated in the figure.

What the chemist requires in his system of formulation is something, not which he can *measure*, but which he can *count*—counters, in short. Such numerical counters he possesses in valencies, in co-ordination numbers. He may be forced to consider the adoption of counters of different kinds, for the purpose of representing essentially different distributions of force; but these counters, if they are to be of general practical value, must neither be too numerous nor of too great variety. Partial valencies, augmented valencies, diminished valencies, virtual valencies, represented by

lines of various sorts, thick, thin, curved, dotted, etc., all tend to complicate formulæ, which lose in obviousness what they gain in definition. The humiliating fact must be admitted that the average man does not succeed in counting quickly and accurately by inspection any larger number of "bonds" than he has fingers on one hand, unless they are appropriately grouped—witness the wrong valencies found, not merely in examination scripts, but even on the printed page. We ought then to set strict limits to the splitting of "bonds" and the issue of fractional valency counters. Fortunately, the physicist has provided us with a new counter, the electron, which has the great merit of being a physical reality, and, moreover, of being an undecomposable magnitude, so that there is no temptation and no possibility of dividing it further. This counter enables us practically to halve ordinary valencies, and so offers many advantages. In the original form given by J. J. Thomson, lines in the formulæ are made to represent tubes of force passing from an electron of one atom to the positive core of another, and since in electrically neutral atoms, for each tube of force which passes out of an atom a return tube must come in, directly or indirectly, one valency line on the old scheme is represented by two tubes of force on the new. The new formulation enables us to write, for example, symmetrical formulæ for benzene and for the carboxyl group, if we so desire, thus :



Or, again, we may represent the valency electrons directly in our formulæ, each atom being equipped with its doublet, sextet, or octet. Such formulæ, or modifications of them, are coming extensively into use when multiple bonds are in question, and there is no doubt that with the electron or electronic tube of force as counter we obtain a more adaptable and more flexible formulation of organic compounds than that afforded by the older valency formulæ, although only with some sacrifice of their simple character.

It will be gathered from what I have said that my plea is for the utmost obviousness of our symbols and formulæ. Their content and connotation may be as rich as we please; the symbols themselves should be of elementary simplicity. But, it may be asked, why should we seek to limit the investigator striving for chemical self-

expression to four whole valencies for carbon if he wants a dozen partial valencies to facilitate his own thought or to convey his exact meaning? And why should he hesitate to adorn his formulae with arrows or positive and negative signs of polarity if he feels the necessity? The answer to such questions must be of a practical nature. The investigator for his own use may employ a symbolism as elaborate and as complex as he chooses, but if he wishes to secure the understanding and sympathy of others he must curb any spirit of exuberance. A system of chemical formulation to have general currency must not be too elaborate. Otherwise, although it effects economy of thought to the expert who devises it, it may demand such a mental strain of the general chemical reader as to defeat a main purpose for which it was planned, namely, the communication of knowledge. I would quote, both with regard to chemical symbolism and to chemical nomenclature, the words used by a character of Henry James concerning literature, "The observer is nothing without his categories, his types and varieties. . . . That's for his own convenience; he has privately a terminology to meet it. . . . But from the moment it's for the convenience of others, the signs have to be grosser, the shades begin to go. . . . Literature, you see, is for the convenience of others. It requires the most abject concessions." Scientific literature is, above all, for the enlightenment and convenience of others, and scientific specialists must be prepared to make concessions to their weaker or less expert brethren. But whether the symbols we use are simple or complicated, we should always be clear as to their true significance, and be on our guard against their distracting our thoughts from the realities which they partly reveal and partly obscure.

OBITUARY NOTICES.

FREDERICK JAMES LLOYD.

BORN 1852; DIED FEBRUARY 8TH, 1923.

F. J. LLOYD was one of the group of younger men who, coming under the influence of the late Augustus Voelcker, then chemist to the Royal Agricultural Society of England, learnt from him the methods of agricultural analytical practice, and, in particular, the application of the principles of agricultural chemistry to the everyday needs of the farmer. This group, comprising Alfred Sibson, John Ruffle, John Hughes—all now deceased—and H. H. B. Shepherd, Alfred Smetham, Bernard Dyer, and J. A. and E. W.

Voelcker, still with us, qualified in this way either to start in analytical practice on their own account, or to become advisers to one or other of the agricultural societies and organisations which then began to spread through the country. Lloyd was one of these, and his after-work was associated mainly with two such Societies, the Bath and West of England Agricultural Society and the British Dairy Farmers' Association.

Born in 1852, Lloyd was educated at Bristol Grammar School, and, coming to London in 1870, he, through the introduction of his cousin, Mr. H. M. Jenkins, then Secretary of the Royal Agricultural Society of England, obtained a post in the late Dr. Voelcker's private laboratory. Leaving this after four years, he went as assistant to the late Sir Thomas Stevenson at Guy's Hospital, and, on the Royal Agricultural Society opening their own laboratory at Hanover Square in 1881, Dr. Voelcker again took him as senior assistant there. Here he remained until autumn, 1883, when he started an analytical practice on his own account in the City of London.

From that time Lloyd's work was concerned mainly with the dairying interest, and, becoming chemist to the British Dairy Farmers' Association in 1885, he continued his active interest on behalf of that body until his death. He was, in this way, responsible for the extensive series of analyses required in connexion with the Dairy Shows annually held at the Agricultural Hall, a work of no small moment or concern. But Lloyd's work was much more than mere routine. He took particular interest in questions of animal nutrition, and contributed to the *Journal of the British Dairy Farmers' Association* a number of papers bearing on this subject. Further, in his association with the Bath and West of England Agricultural Society, of whose *Journal* he was for a number of years co-editor, he carried out extensive investigations both on cheese-making, in relation chiefly to the chemical points involved, and on the manufacture of cider. His work on this latter subject, begun at Glastonbury in the year 1893, did a great deal to put the cider industry on a more scientific basis, and it was indeed the starting point of the research work subsequently so greatly developed at the Agricultural and Horticultural Research Station, Long Ashton, Bristol, by Mr. B. T. P. Barker.

Lloyd held several appointments as agricultural analyst under the Fertilisers and Feeding Stuffs Act, and was a prominent member of the Central Chamber of Agriculture, interesting himself in all matters of a chemical nature affecting the farming industry.

He was quite a good chemist, an accurate analyst, and a hard worker. He possessed a sound knowledge of agricultural chemistry,

and for some years acted as abstractor for the Chemical Society. He published in 1884 "Science of Agriculture" (Longmans), the outcome of lectures which he had given in his capacity of lecturer on Agriculture at King's College, London. Of his scientific work, however, it must be said that it never obtained for him the recognition which it deserved, and others built up largely on the foundations which he had laid.

Peculiarities of temperament and a certain aggressiveness stood much in his way and made his life a chequered and hard one, for he never succeeded in establishing a really good analytical practice, and his later years were attended by much anxiety. At the same time, he was a man who ever held the highest ideals as to the dignity of the chemical profession, and, whether in the Institute of Chemistry (of which he was a Fellow), or at the Farmers' Club (at which he was often a capable contributor to the discussions), he never failed to uphold these views and to impress that the profession of chemistry should occupy a more important position, and be more extensively made use of in the pursuit of agricultural and other industries.

Lloyd died, after a very brief illness, on February 8th at the age of seventy.

J. A. VOELCKER.

GEORG LUNGE.

BORN SEPTEMBER 15TH, 1839; DIED JANUARY 3RD, 1923.

By the death of Professor Lunge, on January 3rd of this year, the Society has lost one who for upwards of fourteen years had been an Honorary Fellow.

Georg Lunge was a native of Breslau, and was born on September 15th, 1839, consequently he was in his eighty-fourth year at the time of his death. His higher education was received at the University of his native town. After graduating as Doctor of Philosophy, Lunge migrated in 1859 to the University of Heidelberg, where, at that time, Bunsen and Kirchhoff were actively engaged in those researches which laid the foundations of spectrum analysis, and where, but a short time previously, laboratory facilities had been improved by the introduction of the now so familiar appliance the Bunsen burner.

By 1862, Lunge had determined to embrace an industrial career, and started a small factory for the manufacture of artificial manures; this enterprise proving unsatisfactory, he, in 1864, came to England and remained in this country for some twelve years. For a part of this period he was engaged as chemist in the tar distillery of Messrs. Major & Co., at Wolverhampton. Later, with the intention

of entering the British heavy chemical industry, he went to the Tyne, where, at that time, some twenty-six alkali works were in full operation. His first attempts in this direction do not appear to have been very encouraging, but ultimately he secured the appointment of chemist and works manager to the Tyne Alkali Company, a small works at South Shields. In this capacity he remained on Tyneside until 1876, when he relinquished the post in response to the call to the Professorship of Chemical Technology in the Polytechnikum of Zurich, rendered vacant by the death of Emil Kopp.

In this position Lunge found a sphere more congenial to his genius, and one in which his profound and extensive knowledge, his practical experience, and tireless energy found full scope. Lunge's success as a teacher, his investigations and writings, created such a reputation that students from far and near, who desired to equip themselves for a career in industrial chemistry, were attracted to Zurich to study under a teacher who was a recognised authority. In 1907, Lunge resigned the post he had filled for thirty-one years. Two years after his retirement a medal was struck to celebrate the seventieth anniversary of his birthday, with his portrait on the obverse, and the reverse representing him at work with his nitrometer and volumeter, devices which have materially extended the use of gasometric methods in quantitative analysis.

The titles of his numerous papers contained in the Royal Society's catalogue show Lunge to have been an exceptionally active worker. A large proportion of these publications deal with technical methods of procedure, and constitute a special service to analytical chemistry. It is interesting to note that his two chief treatises, namely, "Coal Tar and Ammonia" and "Sulphuric Acid and Alkali," are concerned with those branches of chemical industry of which he had obtained practical experience whilst resident in this country. The former was published in 1867, and the latter in 1878; both have passed through several editions, have been very materially added to, and these together with the work on technical chemical analysis are universally recognised as reference books indispensable to the technical chemist. His smaller works, "the Technical Chemist's Handbook" and "Technical Gas Analysis," may also be regarded as valuable contributions to the advancement of industrial chemistry, inasmuch as they contain descriptions of trustworthy and exact methods for the analysis of products and the control of processes of manufacture.

During his residence on Tyneside, Lunge did much to promote an interest in the scientific aspect of the chemical industries of the

district, and was one of the active workers in the Newcastle Chemical Society, which was founded in 1868, with Mr. Isaac Lowthian Bell (afterwards Sir Lowthian Bell, Bart.) as its first President. Of this Society Lunge was elected President in 1872. When this Society, in 1883, became the Newcastle Section of the Society of Chemical Industry, Lunge, an original member of the last-named Society, was enrolled as a member of the Newcastle Section, with which he maintained a close association until the time of his death. His interest in its welfare was shown by using its *Proceedings* as a medium for the publication of many of his valuable contributions, as also in his ready willingness to subscribe, as occasion arose, to special funds raised by the members of the Section.

In 1889, Lunge, on the invitation of the Liverpool Section, delivered the first of the lectures, inaugurated to commemorate the valuable services of Dr. Hurter to chemical industry; "Impending Changes in the Development of Industry and particularly of the Alkali Industry" formed the subject of the lecture on this occasion.

Amongst the distinctions conferred on Lunge in recognition of his great services, the Honorary Degree of Dr. Ing. of the Technische Hochschule, Karlsruhe, should be mentioned. Surely a most fitting exercise of the new powers and privileges granted to the authorities of such Institutions.

P. P. B.

ALEXANDER SMITH.

BORN SEPTEMBER 11TH, 1865; DIED SEPTEMBER 8TH, 1922.

ALEXANDER SMITH was born on 11th September, 1865, in Edinburgh, where his father was a well-known musician. He was educated at the Collegiate School, and in 1882 he entered the University of Edinburgh as a science student. He studied chemistry under Crum Brown, mathematics under Chrystal, and natural philosophy under Tait. Although chemistry was his main subject, he spent some time at research in physics under Tait's direction. In 1886, he graduated as B.Sc., and during the three following years pursued the study of chemistry in the University of Munich, where he worked in Baejer's laboratory, chiefly under the direction of Claisen. After graduating as Doctor of Philosophy in 1889, he returned to Edinburgh and was appointed assistant in the chemistry department of the University. This appointment he held for one year only, for during a trip to the United States in the summer vacation of 1890 he was offered and accepted the Chair of Chemistry and Mineralogy in Wabash College, Crawfordsville, Indiana. During his short tenure of the Chair the number of undergraduates studying

chemistry more than doubled. In 1894, he joined the staff of the newly-founded University of Chicago with the rank of Assistant Professor, soon raised to that of Associate Professor. In 1903, he was appointed to an independent Chair and was made Director of General and Physical Chemistry. He remained in Chicago until 1911, when he received the appointment of head of the Department of Chemistry in Columbia University, New York, a position which he retained until his retirement through illness in 1921.

As a teacher and organiser of instruction in chemistry Alexander Smith stands pre-eminent. The qualities which later gained him so high a reputation were observable in his teaching in Edinburgh when he was a young man of four-and-twenty. A course of lectures which he delivered then on organic synthesis stimulated the interest of his hearers in an extraordinary degree. He had an easy, fluent style of delivery, knew intuitively how to keep the attention of the audience he was addressing, and had the invaluable gift of selecting and impressing the essential points of his subject. In America he devoted much thought to the manner of presentation of chemistry to students of various types and of different ages, ranging from secondary scholars to post-graduate workers, and, fortunately for his fellow-teachers, he embodied his principles in an admirable series of text-books. As chairman of a sub-committee of the National Education Association of the United States, he prepared in 1899 an outline course in chemistry for secondary schools, which is now the basis of the chemistry work of the secondary schools throughout America. His "Laboratory Outline of General Chemistry," issued in the same year, was the precursor of the corresponding theoretical work, the "Introduction to General Inorganic Chemistry," which, appearing in 1906, met with immediate acceptance in the English-speaking world, and has since been translated into the language of almost every country where scientific study is pursued. His other educational works of later date were characterised by the same originality of thought and orderliness of method. It is a testimony to the esteem in which his text-books were held that one of them was translated into German by Professor Haber. He may without exaggeration be said to have revolutionised the teaching of chemistry in America.

Smith at the outset of his career was an organic chemist, and the ten papers which he published between 1889 and 1902 are exclusively concerned with organic topics, chiefly the chemistry of diketones, the benzoin synthesis, and, generally, the action of potassium cyanide as a condensing agent. As a result of his teaching work in Chicago, and his critical review of the matter and mode of presentation of elementary inorganic chemistry, he gradually

became engrossed in this fresh field, and his research after 1902 is exclusively inorganic and physico-chemical. A series of papers on amorphous sulphur is of outstanding merit. At the time his investigations were begun, the published observations on the behaviour of melted sulphur were full of apparent inconsistencies and could not be formulated in harmony with physico-chemical theory. He investigated the relationship between the freezing point of the melt and the proportion of amorphous sulphur contained in it, and showed that Raoult's law was rigorously obeyed, thus establishing the existence of liquid amorphous sulphur dissolved in but distinct from the liquid "soluble" sulphur. He investigated the problem why melted sulphur kept at a constant temperature should give on chilling varying proportions of amorphous sulphur. The variation he proved to be due to catalysts which accelerated or retarded the change from amorphous to soluble sulphur. As one of these catalysts was sulphur dioxide, always present in varying proportions in ordinary experiments, the inconsistencies in previous observations received a simple explanation. The true equilibrium proportions of amorphous sulphur at various temperatures were determined, and the conclusion established that the two forms of sulphur in the liquid state behaved with respect to each other as dynamic isomerides. He then directed his attention to precipitated sulphur and showed that, when first set free, precipitated sulphur consists of minute drops of liquid amorphous sulphur. In alkaline, neutral or feebly acid solutions these change wholly to crystalline sulphur. In presence of strong acids the amount of amorphous sulphur in the final product is proportional to the concentration of the acid. Finally, he subjected the melting- and freezing-points of the various forms of sulphur to revision and determined the correct values, in harmony with the theory.

In conjunction chiefly with A. W. C. Menzies, now Professor of Chemistry at Princeton, Smith published a long series of papers on vapour pressures, the experimental work being of a very high order of accuracy. A simple method—that of the "submerged bulblet"—was devised by means of which the vapour pressures of liquids and solids and the boiling points of liquids could be determined with the use of minute amounts of material. Then forms of apparatus were described for the exact measurements of vapour pressures, which were named the static and dynamic "isotenscopes" respectively, and tested by determination of the vapour pressures of water and benzene, the results agreeing with the best previous determinations. Since for the purpose of a research on calomel vapour an exact knowledge of the vapour pressures of

mercury up to high temperatures was required, a series of accurate determinations for the metal between 250° and 435° were made and values obtained which entirely supersede the inconsistent observations of previous investigators. The vapour pressures of mercurous chloride, mercury, and mixtures of the two, were measured and by the application to the data of the ordinary law of chemical equilibrium there was deduced the result that the vapour consists wholly of mercury and mercuric chloride. Proceeding from this deduction it was found that mercurous chloride when rigorously dried, so as to prevent dissociation, has no measurable vapour pressure even at high temperatures.

The problem next considered was the dissociation of the ammonium halides. Vapour density determinations for ammonium chloride had shown that whilst the rigorously dried salt had in the vaporous state a density corresponding with the formula NH_4Cl , it was completely dissociated into ammonia and hydrochloric acid at 350° if a trace of moisture were present. It was pointed out that this dissociation value had been obtained in an unsaturated vapour. For the saturated vapour at the same temperature the degree of dissociation did not exceed two-thirds. The other ammonium halides were found to be considerably less dissociated. An investigation was undertaken to explain the paradoxical fact that the vapour pressure of ammonium chloride is at a given temperature the same whether dried or undried, although in one case the vapour is highly dissociated and in the other not at all. Although the problem was not solved, the untenability of hypotheses which had been put forward by other investigators for its explanation was clearly demonstrated.

Smith's research work is characterised by the same qualities of clear insight, logical development, and scrupulous accuracy as we find in his work as a teacher. The merit of both was recognised officially by his appointment to the Presidency of the American Chemical Society in 1911, by his election to membership of the National Academy of Sciences, by the award of the Keith Prize and Medal by the Royal Society of Edinburgh in 1912, and by the degree of LL.D. which was conferred on him by the University of Edinburgh.

Smith's personality was most attractive. His interesting and amusing conversation, and his hearty, infectious laugh will long remain in the memory of his friends. Always of boundless energy, he overstrained himself during the war period, and insisted in spite of medical warnings on continuing his writing and on carrying on his huge department with a depleted staff. A complete breakdown, complicated by a serious operation, followed, and as his health did

not improve after a year's leave of absence he was obliged to relinquish his Chair. Becoming gradually weaker, he died in his native town on September 8, 1922.

Smith married in 1905 Mrs. Sara Bowles of Memphis, Tennessee, and is survived by her and by two children, a son and a daughter.
J. W.

JOKICHI TAKAMINE.

BORN SEPTEMBER 23RD, 1855; DIED JULY 22ND, 1922.

JOKICHI TAKAMINE was born in Takaoka, Japan, on September 23rd, 1855, and was the eldest son of a physician, Soichi Takamine. At an early age he received a Government scholarship, and was educated at the Imperial College of Engineering, now the Imperial University of Tokio. After graduation in 1878, he was sent by the Government to Great Britain, and studied applied chemistry for three years in Glasgow at the University and Andersonian College. During this period he collaborated with Prof. E. J. Mills in a research on the absorption of weak reagents by cotton, silk, and wool, which was published in this *Journal* in 1883. He returned to Japan by way of America, and was at once employed by his Government in many important capacities, among these being those of Commissioner to the International Industrial Exposition at New Orleans, the first of a long list of similar offices, chief chemist to the Department of Agriculture and Commerce, director of the Government Chemical Laboratory and Commissioner for Trade Marks and Patents for the Empire of Japan. He also revisited Europe and America for the purpose of making industrial observations. On his return, he resigned his Government appointment and established the Tokio Artificial Fertiliser Co., the first to manufacture superphosphate in Japan.

About 1891, Takamine settled in America, at Clifton, New Jersey, and set up a private laboratory, where most of his subsequent work was carried out. Takamine was held in high honour both in official and learned circles in Japan. He received the degree of Doctor of Engineering in 1899 and of Doctor of Pharmacology in 1904. He was made a member of the Orders of the Sacred Treasure and of the Double Rays of the Rising Sun, and subsequently rose several steps in rank. Perhaps his greatest distinction was his appointment by Imperial Decree as one of the sixty members of the Imperial Academy of Science in Japan.

Throughout his career in America Takamine was intensely interested in fostering good relations between the countries of his

birth and of his adoption. To the accomplishment of this object he contributed by way of the formation of an American-Japanese society and by his constant participation as commissioner or delegate in exhibitions and congresses. He kept open house for Japanese visitors to America, and was regarded by his countrymen as an unofficial Japanese Ambassador. He died on July 22nd in New York, aged sixty-seven years.

Takamine was active in many branches of applied chemistry, but his name is chiefly associated with the commercial preparation of taka-diastrase and of adrenaline.

The saccharification of starch in the Japanese process of brewing Saki from rice is brought about by the diastase of a mould, usually *Aspergillus oryzae*. The properties of this diastase were examined in 1881 by Atkinson (*Proc. Roy. Soc.*, 1881, **32**, 299), who found that by its action on starch glucose was produced. For use in the brewing process steamed rice is inoculated with material bearing the matured spores of the mould (*moyashi*) and incubated at 30° or about seventy-six hours. It is then known as *kōji* and has about one-half to one-fourth of the diastatic power of malt. Takamine's process (*J. Soc. Chem. Ind.*, 1898, **17**, 118) consisted in producing a more concentrated or taka-*kōji* (*taka* in Japanese means *high*) by growing the mould on wheat bran, a product being obtained of about four to eight times the diastatic power of the ordinary *kōji*. Extraction with water removes the whole of the diastase, which can be precipitated from an extract containing 20 per cent. of solids by the addition of 4–5 volumes of alcohol. The dried precipitate forms the taka-diastrase of commerce. It was pointed out by Takamine that this product has a much greater liquefying power for starch paste than malt diastase of equal saccharifying power. It has found extended application in medicine, baking, the preparation of cereal foods, and in the textile industries.

Adrenaline was obtained in crystalline form in 1900 from the aqueous extract of suprarenal glands by evaporation with precautions to avoid oxidation, followed by precipitation by making alkaline and adding an ammonium salt or passing a current of carbon dioxide (*Amer. J. Pharm.*, 1901, **73**, 523).

Takamine was also the inventor of a process for extracting cobalt oxide from Japanese manganese ores for use in the pottery industry and of a method for the recovery of glycerol from printer's rollers.

The writer is indebted for the main facts of Takamine's career to obituary notices in the *Journal of the Society of Chemical Industry* (1922, **41**, 464r), and in the Japanese medical journal *Ikaisho*, published in Tokio.

A. HARDEN.

having the energy and ability which Tschugaev displayed are sufficiently rare in any country; and Russia least of all could afford to lose him.

T. M. LOWRY.

FRANK EDWIN WESTON.

BORN 1867; DIED JANUARY 4TH, 1923.

THE death of Frank Edwin Weston removes an indefatigable worker from the field of pure and applied chemistry, and deprives our country, and especially London, of one of the finest teachers of chemical science of our day. Born in 1867, he received his scientific training at St. John's College, Battersea, and at Birkbeck College, taking supplementary courses at King's College and University College, London, and graduating with first class honours in chemistry (B.Sc.) in 1900. He joined the staff of the Regent Street Polytechnic in 1893, and in 1911 was made head of the chemical department, which position he retained until his death. At the Polytechnic he will long be remembered for his ceaseless activities, his organising ability, and his clear-sighted judgment. Many generations of students will remember with gratitude the lucidity of his teaching, the simplicity of his methods, and the intense personal interest which he took in each member of his classes.

Previous to the war Weston published original researches, amongst which may be mentioned the detection of sodium sulphite in the presence of sulphate and thiosulphate (1908); the crystallisation of explosives (1908); the action of aluminium powder on silica, boric anhydride, and on carbon (1908); the heats of combustion of aluminium, calcium, and magnesia (1909); a modified apparatus for the estimation of nitrogen (1909); and thermic reactions in a vacuum (1911). Most of these were in collaboration with H. Russel Ellis.

During the war Weston carried out an important investigation on alloys for aeroplane construction, for the Air Ministry, and with others, prepared considerable quantities of the drugs novocaine and β -eucaine, which were in great demand by the military medical authorities. In connexion with this he found that the ordinary method for the preparation of ethyl bromide was very inefficient, and worked out an alternative procedure, which gave a high percentage yield (published in the *Transactions*, 1915, 107, 148⁹).

He was the author of several publications on chemical subjects, including a small book of great value to students of chemistry,

entitled "The Detection of Carbon Compounds," which had a great vogue and has been translated into French, Spanish, and Italian. At a later date he collaborated with the present writer in producing a two-volume work, entitled "Technical Handbook of Oils, Fats and Waxes."

Although in recent years hampered by ill health, his activities continued to the last, and many of the general public, outside scientific circles, will remember him in connexion with his work on the detergent value of colloidal clays, of which notices appeared in the daily Press. He was elected a Fellow of the Institute of Chemistry in 1918.

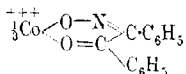
Weston was a man of strong personality, who made a deep impression on those with whom he came into intimate contact. His somewhat loud voice and brusque manner only imperfectly concealed his kindly and unselfish disposition. A ruthless opponent of all sham and superficiality, he was himself a consistently zealous and conscientious worker and a man of stainless honour and integrity.

He leaves a widow and one son, Ramsay, whom he lived to see gain the distinction of a first class honours degree in science as late as a few weeks ago.

PERCIVAL J. FRYER.

formed, but there appeared to be little or no tendency to the formation of tetra-, hepta-, or octa-atomic ring systems (*J. pr. Chem.*, 1907, [ii], 75, 153). Representatives of the last two types have been prepared by Tschugaev himself (*Z. anorg. Chem.*, 1905, 46, 144), by Duff (*T.*, 1921, 119, 385), and by Price and Brazier (*T.*, 1915, 107, 1373); but the general principle still holds good that co-ordination is favoured in a very remarkable way when it is possible to construct either a saturated ring system containing five atoms, or a conjugated ring system containing six atoms, the co-ordinated metal being in each case counted as a member of the ring.

The best known of Tschugaev's discoveries in this field was that of the nickel derivative, $\text{Ni}(\text{O}:\text{N}:\text{CMe}:\text{CMe}:\text{N}:\text{OH})_2$, of dimethylglyoxime, which has found an important application in analytical chemistry, but this compound is itself an example of a complex containing a seven-membered ring. Tschugaev also found that the oximino-ketones behave in general like nitro- α - β -naphthol in yielding very stable derivatives with cobalt, and prepared a series of analogous compounds of iron, nickel, and palladium, all of which were distinguished by their great stability, abnormal colour, and absence of ionic reactions of the metal. These compounds are an important illustration of Tschugaev's principle, since their formation is associated with the development of a conjugated ring-system containing six atoms as shown in the formula



Tschugaev came to London in 1909 as one of the Russian representatives to the International Congress; he was a member of a group which also included Walden, Ipatiev, and Kistiakowski. He contributed a paper on anomalous rotatory dispersion to a general discussion on optical rotatory power held before the Faraday Society on March 27th, 1914, although on this occasion he was not able to attend in person. This paper was distinguished by a clear recognition of three distinct causes which might independently give rise to anomalous dispersion.

Tschugaev's death was directly due to the deplorable conditions following the revolution in Russia. Life in Petrograd had become so difficult that he had moved his wife and children out to Wologda; and was during one of his visits to Wologda that he acquired the disease which brought about his death. His loss was a serious one for chemistry in general; to Russian chemistry it was a real disaster, since even under favourable conditions research workers

having the energy and ability which Tschugaev displayed are sufficiently rare in any country; and Russia least of all could afford to lose him.

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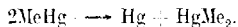
PERCIVAL J. FRYER.

CIX.—*An Electrolytic Method for the Preparation of Mercury Dimethyl.**

By JULIAN LEWIS MAYNARD and HENRY C. HOWARD, jun.

DURING the past year, one of us has frequently had occasion to prepare considerable quantities of mercury dimethyl. The five methods then available for its preparation (see F. C. Whitmore, "Organic Compounds of Mercury," American Chemical Society Monograph Series, pp. 85—86) were known to give poor yields, and therefore, since the excellent process employing the Grignard reaction (Marvel and Gould, *J. Amer. Chem. Soc.*, 1922, **44**, 153) has not yet appeared, it was decided to attempt to develop a more satisfactory means of synthesis.

When solutions of the methylmercuric halides in liquid ammonia, in water, and in alcohol are electrolysed, the complex MeHg - is deposited on the cathode in fine black flakes, which decompose completely at the ordinary temperature into mercury and mercury dimethyl (Kraus, *ibid.*, 1913, **35**, 1740):



Thus, in view of the ease with which this reaction proceeded at the ordinary temperature, the electrolysis of a concentrated aqueous solution of a methylmercuric salt appeared to afford a simple mean for the preparation of the mercury dialkyl. Electrolysis of liquid ammonia solution was avoided because of various mechanical difficulties, whilst an alcoholic solution was not considered because of the very low order of its conductivity.

In order to determine the most suitable salt for use as the electrolyte in this preparation, conductivity measurements were made on aqueous solutions of various methylmercuric salts, and on the free base, $\text{MeHg}\cdot\text{OH}$, recently isolated by one of us (Sneed and Maynard, *J. Amer. Chem. Soc.*, 1922, **44**, 2042). A few of the results are given in the following table; temperature 25° , concentration 0.1N:

Compound	$\text{MeHg}\cdot\text{OH}$	$\text{MeHg}\cdot\text{OAc}$	$(\text{MeHg})_2\text{SO}_4$	MeHgNO_2
Equiv. cond.	0.71	4.02	57.40	101.00

The low conductivity exhibited by the base was surprising inasmuch as compounds of the type $\text{RHg}\cdot\text{OH}$ have been very generally described in the literature as strong bases. However the weakness of the base as indicated by our conductivity measurements was substantially borne out by the fact that large increase in the equivalent conductivity of methylmercuric salts at dilution even greater than 1000 litres indicated a considerable degree of

* A preliminary report on this article was made to the American Chemical Society at its Birmingham, Alabama, meeting in April, 1922.

hydrolysis. Thus, for example, the equivalent conductivity of the nitrate at various dilutions at 25° was found to be as follows :

Dilution in litres	10	50	250	1250	6250
Equiv. cond.	101	116	129	150	162

Again, the weakness of methylmercuric hydroxide as a base was clearly shown by the ionisation constant calculated from the degree of hydrolysis of the nitrate. The constant was found to be 3.9×10^{-11} at 25°. The commonly accepted value for aniline at the same temperature is 5×10^{-10} . As was to be expected, methylmercuric hydroxide reacted acid towards phenolphthalein.

Work done by one of us* has indicated that ethylmercuric hydroxide is likewise very slightly ionised, and a preliminary report on *n*-butylmercuric hydroxide has shown that compound to be correspondingly weak base.† Therefore, despite statements to the contrary found in text-books of organic chemistry and in the literature generally, it was concluded that alkyl mercury bases of the type $\text{RHg}\cdot\text{OH}$ are indeed very weak. That the basis for previous statements to the contrary is unfounded is shown by the fact that the recent preparation of methylmercuric hydroxide (Sneed and Maynard, *loc. cit.*), ethylmercuric hydroxide,‡ and the corresponding *n*-butylmercuric derivative marks the first instances of the isolation *in the pure state* of aliphatic mercury bases of the type $\text{RHg}\cdot\text{OH}$. The reputed strength of these bases has evidently been inferred from a single instance in which a solution containing ethylmercuric hydroxide displaced ammonia from its salts, and precipitated the hydroxides of the heavy metals (Dunhaupt, *Annalen*, 1854, **92**, 381).

It was recognised very early in the course of this study that the low conductivity of aqueous solutions of methylmercuric salts presented a decided difficulty in the development of an electrolytic method for the preparation of mercury dimethyl. Methylmercuric chloride, bromide, and iodide were unsuitable for use as electrolytes because of their slight solubility in water; the use of the more soluble salts of the active acids, for example, the nitrate and phosphate, was precluded because of the presence in their solutions of an undesirable quantity of hydrogen-ion due to hydrolysis.

Attention was then directed to the methylmercuric salts of weak acids and to the base itself. As was to be foreseen from the low conductivity of the latter, preliminary electrolytic experiments

* Unpublished results (J. L. M.).

† W. V. Evans and Louise Otis, *The Ionisation of n-Butylmercuric Hydroxide*. A preliminary report presented before the American Chemical Society at the Birmingham, Alabama, meeting, April, 1922.

‡ Isolated by Maynard. Results unpublished.

showed the impossibility of obtaining any considerable quantity of mercury dimethyl within a reasonable time. It was found impossible to isolate the carbonate because of its instability, for after an excess of carbon dioxide had been passed into a solution of methylmercuric hydroxide, all attempts to concentrate the solution resulted in the complete removal of this gas, so that only the base remained. This behaviour was to be expected, and it further confirmed the conclusion that methylmercuric hydroxide is a weak base.

Experiments were next carried out on methylmercuric acetate, a salt which is very soluble in water, and easily prepared from methylmercuric iodide (Sneed and Maynard, *loc. cit.*). When aqueous solutions of the acetate were electrolysed, mercury dimethyl was formed at the cathode, but owing to the low conductivity of the solutions the process was very slow. Since it was known that pyridine increases the conductivity of certain slightly ionised salts such as mercuric chloride (Gmelin-Kraut's "Handbuch der anorganischen Chemie" (1914), Band V, Abt. 2, pp. 920--921), we tried its effect on solutions of methylmercuric acetate. The desired increase in conductivity was so considerable as to make rapid electrolysis possible. The influence of varying amounts of pyridine on the conductivity of solutions of methylmercuric acetate is shown in the following table:

Specific conductivity of 0.05N-McHg-OAc at $25^\circ \pm 33.7 \times 10^{-5}$.

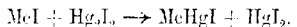
Mols. of pyridine added per mol. of McHg-OAc...	0.1	1	2	4
Sp. cond. of solutions	147×10^{-5}	232×10^{-5}	271×10^{-5}	277×10^{-5}

A maximum specific conductivity of less than 2×10^{-5} was exhibited by aqueous solutions containing pyridine in concentrations equivalent to the quantities present in the above-mentioned solutions of methylmercuric acetate. The very marked increase in the conductivity of the electrolyte in the mixed solvent seemed to indicate that an interaction had taken place, and that highly conducting complexes had been formed. In partial support of this conjecture it will be noted that a conductivity curve plotted from the values given would show a very sudden flattening after the addition of two mols. of pyridine.

Thus, with the desired increase in conductivity of methylmercuric acetate in the mixed solvent, it became possible to prepare quantities of mercury dimethyl without difficulty. The mixed solvent did not dissolve the dialkyl, so that as it dropped from the cathode it formed a layer at the bottom of the cell, and could be drawn off readily without disturbing the progress of the electrolysis. A material yield exceeding 90 per cent. and a current efficiency of 90 per cent. combine to make the process satisfactory from the

point of view of the organic chemist. After the simple electrolytic cell has been constructed, the method compares favourably in point of time with the synthesis effected by means of the Grignard reaction (Marvel and Gould, *loc. cit.*). Inasmuch as test runs have shown that mercury diethyl and mercury dipropyl can be prepared by the electrolysis of the corresponding ethyl- and propyl-mercuric acetates, it is suggested that this method might be extended to include the preparation of the other liquid mercury dialkyls.

Methylmercuric iodide necessary for the preparation of methylmercuric acetate has recently been made more available by a rapid method of preparation. It has been found that methyl iodide reacts readily with mercurous iodide at 75° when exposed to the light of the electric arc : *



Methylmercuric iodide has heretofore been prepared by allowing mercury to stand in the sunlight with methyl iodide (Frankland, *Quart. J. Chem. Soc.*, 1850, **3**, 322; *Annalen*, 1851, **77**, 225; 1853, **85**, 361). The acetate may in turn be obtained from the iodide in excellent yield by the use of several methods lately worked out (Sneed and Maynard, *loc. cit.*), and also by the addition of mercuric acetate to a well-stirred, hot, aqueous suspension of methylmercuric iodide. The latter method is preferable when it is not desired to isolate the methylmercuric acetate.

EXPERIMENTAL.

The electrolyte employed in this preparation consisted of an aqueous 25 per cent. solution of methylmercuric acetate to which pyridine was added in the ratio of two mols. of the latter to one mol. of the organomercuric salt.

The cell was constructed of a cylindrical glass vessel tapering at the lower end, and fitted there with a stop-cock through which the mercury dimethyl was drawn off as desired. A porous cup suspended in the centre of the glass vessel served as the anode compartment. The cathode consisted of a sheet of smooth platinum foil, supported concentrically about the porous cup at a distance of a few mm. therefrom. The anode was made up of two graphite rods. The entire cell was water-jacketed so that during electrolysis the temperature could be maintained between 30° and 40°.

At the beginning of the electrolysis a potential of 30—35 volts produced a current of 2.5 amps. This of course fell off as the concentration of the methylmercuric salt in the solution decreased. The area of the cathode, considering only the side nearest the

* Unpublished results obtained by Maynard.

anode to be active, was 138 sq. cm. The cathodic current density at the beginning of the electrolysis was therefore 1.8 amps./sq. cm. The total area of the anodes was 62.8 sq. cm., and hence the anodic current density was 4 amps./sq. cm.

The details of a typical run are as follows: The electrolyte consisted of 106.5 grams of methylmercuric acetate in the form of a 25 per cent. aqueous solution with two mols. of pyridine added per mol. of acetate. An average current of 1.67 amps. flowed over a time of 2 hours 10 mins.; the total number of ampere-hours was 10.64. Thus, the current yield demanded by theory was 46.1 grams of HgMe_2 ; an actual yield of 41.4 grams set the current efficiency at 90 per cent. The actual yield amounted to 92 per cent. of the theoretical material yield of 45.1 grams.

Summary.

1. Alkyl mercury bases of the type RHg-OH have been shown to be very weak bases.
2. An electrolytic method for the preparation of mercury dimethyl has been described.

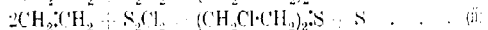
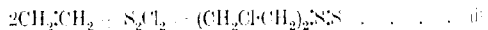
PRINCETON, NEW JERSEY.

[Received, January 8th, 1923.]

CX.—Action of Sulphur Monochloride on Mercaptans.

By GOPÁL CHANDRA CHAKRAVARTI.

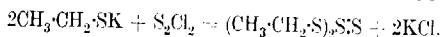
THE present investigation was undertaken with a view to study systematically the nature of the products obtained by the interaction of real and potential mercaptans with sulphur monochloride. A good deal of work has been done to elucidate the reaction between sulphur monochloride and the unsaturated hydrocarbons; Guthrie (*Quart. Journ. Chem. Soc.*, 1860, **12**, 116; 1861, **13**, 134; *Annalen* 1861, **119**, 91; 1862, **121**, 110); Pope (*J. Soc. Chem. Ind.*, 1919 **38**, 469R); A. G. Green (*ibid.*, 469R); Conant, Hartshorn, and Richardson (*J. Amer. Chem. Soc.*, 1920, **42**, 585); Gibson and Pope (T., 1920, **117**, 271); Mann, Pope, and Vernon (T., 1921, **113**, 634). The chief and interesting point of research in most of them has been the stability of the bivalent sulphur atom of sulphur monochloride when it reacts with other compounds. By the action of sulphur monochloride on ethylene, Green (*loc. cit.*) seems to have obtained the disulphide (i).



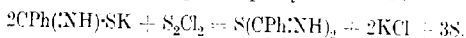
Pope (*loc. cit.*), however, suggested that the second sulphur atom remained in "some sort of pseudo-solution"; and Gibson and Pope (*loc. cit.*) represented the reaction as taking course (ii).

The last view was placed on a firm experimental basis by Harrison (T., 1921, 119, 329). But recently Naik (*ibid.*, p. 329) has shown that in the synthesis of the dithio-ketones and dithio-ethers the sulphur atom in question is not eliminated and the products obtained, which are formulated as $R_2C(S)S$ and $R_2S(S)S$, are exceedingly stable. Smythe and Forster (T., 1910, 97, 1195) obtained benzyl tetra-sulphide from benzyl mercaptan and sulphur monochloride, the sulphur atom remaining intact. In the present investigation the products obtained, although they have such complex structures as $S(SR)_2$, are also remarkably stable, and the sulphur atom retains its position firmly in the molecule. It would thus seem that the stability of the bivalent sulphur atom depends entirely on the nature of the compounds with which it enters into combination.

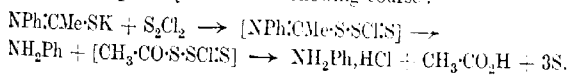
Rây and Das (T., 1922, 121, 323) have found in chloropierin a reagent capable of distinguishing a real from a potential mercaptan. They find that when chloropierin reacts with a real mercaptan no sulphur is eliminated, but when it acts on a potential mercaptan sulphur is invariably separated either partly or completely. In the case of sulphur monochloride the same behaviour has been observed :



Ethyl mercaptan being a real one, there is no separation of sulphur. But with thiobenzamide sulphur is partly eliminated :

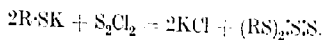


Sometimes, when the strain is very great in the process of tautomerisation to the "thiol" form, the molecule is completely ruptured. In such cases, products are obtained which are totally deprived of their sulphur, for example, thioacetanilide is completely decomposed and the main product which is isolated is aniline hydrochloride. The reaction possibly takes the following course :



Thus sulphur monochloride, like chloropierin, can be utilised in differentiating real and potential mercaptans.

The compounds described in this paper are prepared by the interaction of the alkali salts of mercaptans, dissolved or suspended in alcohol, and sulphur monochloride, dissolved in light petroleum. The reaction with a real mercaptan proceeds according to the equation



The now generally accepted formula of sulphur monochloride, $SSCl_2$, has been adopted throughout this investigation.

EXPERIMENTAL.

*Real Mercaptans.**

Product from Ethyl Mercaptan, $\text{S}_2\text{S}(\text{SEt})_2$.—Sodium mercaptide (prepared by the action of finely divided sodium on ethyl mercaptan, dissolved in anhydrous ether) was dissolved in an excess of absolute alcohol at about 60° and gradually treated with a dilute solution of sulphur monochloride in light petroleum (b. p. $80\text{--}100^\circ$) with constant shaking until sodium chloride was no longer precipitated. The yellow oil that separated was repeatedly washed with water and its ethereal solution heated on the water-bath to remove ether. The oil was next distilled with steam, the distillate extracted with ether, and the golden yellow, mobile oil remaining after removal of the solvent finally dried in a vacuum over sulphuric acid. It boils at $210\text{--}212^\circ$ (Found: C = 26.09; H = 5.41; S = 68.43. $\text{C}_4\text{H}_{10}\text{S}_4$ requires C = 25.80; H = 5.37; S = 68.81 per cent.).

Product from Phenyl Mercaptan, $\text{S}_2\text{S}(\text{SPh})_2$.—To an alcoholic solution of the mercaptan (1 mol.) alcoholic caustic potash was added (1 mol.), followed by sulphur chloride in light petroleum. An oil together with potassium chloride separated out. The oil was washed thoroughly with water, extracted with ether, the ether removed on the water-bath, and the residue repeatedly dissolved in a large excess of ether, filtered, and precipitated by alcohol. The oil thus obtained was heated in the steam-bath for about three hours and finally kept in a vacuum desiccator over-night. It is a yellow oil with offensive odour and is soluble in ether, chloroform, acetone, or benzene, but insoluble in alcohol (Found: C = 59.62; H = 3.86; S = 46.21.† $\text{C}_{12}\text{H}_{10}\text{S}_4$ requires C = 51.06; H = 3.54; S = 45.39 per cent.).

Product from Dithioethylene Glycol, $\text{S}_2\text{S}(\text{S}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{SH})_2$.—When alcoholic caustic potash was added to an alcoholic solution of dithioethylene glycol, colourless needles of the monopotassium salt, $\text{SH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{SK}$, separated (Found: K = 29.85 per cent.). This salt was dissolved in alcohol and treated as before with sulphur chloride. A solid product was obtained which was washed with water and heated under reflux first with absolute alcohol and then

* A few organic tetrasulphides have already been described (Otto, *J. pr. Chem.*, 1888, [ii], **37**, 211; Troeger and Hornung, *ibid.*, 1899, [ii], **60**, 113); the method of preparation adopted in this paper is entirely different.

† It may be necessary to point out that in these compounds the sulphur atoms are linked both to a fatty and to an aromatic and cyclic residue. Carius's method usually gave low results owing to the formation of sulphonic acid. The excess of nitric acid was therefore neutralised with sodium carbonate and the solution evaporated to dryness and fused in a platinum crucible. The melt was evaporated several times with hydrochloric acid and before precipitating with barium chloride. Owing to the presence of a large amount of sodium chloride and undecomposed sodium nitrate the result is generally a little high.

S = 75.47; N = 13.21 per cent.). The above compound was heated under reflux with excess of ethyl iodide for about five hours. The product was extracted with acetone, when a quantity of sulphur remained. After removal of the acetone and crystallisation from alcohol, it melted at 114° (Found: C = 15.42; H = 2.75; N = 4.83; I = 61.43; S = 15.41. $C_2N_2S_3.3C_2H_5I$ requires C = 15.84; H = 2.47; N = 4.63; I = 61.22; S = 15.84 per cent.).

Product from β -Naphthyl Mercaptan, $S(S(C_{10}H_7)_2)_2$.—The yellow precipitate obtained by the interaction of sulphur monochloride and β -naphthyl mercaptan was thoroughly washed with water, dissolved in benzene, heated under reflux with copper powder, and finally precipitated with hot alcohol. It melts between 82–85° (Found: S = 33.02. $C_{20}H_{14}S_4$ requires S = 33.51 per cent.).

Potential Mercaptans.

Thiobenzoic acid gave with sulphur monochloride a crystalline precipitate which was identified as dibenzoyl disulphide. Thiocarbamide, dissolved in alcohol, and an equimolecular quantity of alcoholic potash were shaken with a solution of sulphur chloride. The brown precipitate obtained, which was found to be very rich in sulphur, could not be crystallised and its constitution has not yet been determined. The filtrate was evaporated to dryness and the residue extracted with alcohol. The product after removal of alcohol was purified by passing steam and then twice recrystallised from ether. It melts at 248° (Found: C = 70.07; H = 5.72; N = 12.51; Cl = 10.35. $C_{19}H_{18}N_3Cl$ requires C = 70.48; H = 5.56; N = 12.98; Cl = 10.97 per cent.). On similar treatment, thioacetamide was completely decomposed and aniline hydrochloride was isolated among other products. With sulphur chloride, thiobenzamide gave a precipitate of sulphur. The filtrate was slowly evaporated to dryness and the residue extracted with alcohol. Colourless crystals, m. p. 92°, were obtained (Found: C = 69.49; H = 5.19; N = 11.63; S = 13.43. $C_{14}H_{12}N_2S$ requires C = 70.00; H = 5.00; N = 11.66; S = 13.33 per cent.). Pinacolylthiocarbamide and allylphenylthiocarbamide were decomposed and no product could be isolated in a pure condition. From thioacetamide, colourless needles, m. p. 104°, were obtained (Found: N = 25.60; S = 29.21. $C_7H_{14}N_4S_2$ requires N = 25.69; S = 29.36 per cent.).

In conclusion, the author's best thanks are due to Sir P. C. Ray for his valuable help and kind interest during the progress of the investigation.

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[Received, January 1st, 1923.]

CXI.—*The Oxidising Properties of Sulphur Dioxide.*
Part IV. Molybdenum Sulphates.

By WILLIAM WARDLAW and NORMAN DARBY SYLVESTER.

CHILESOTTI, in a paper on the electrolytic reduction of solutions of molybdic anhydride in hydrochloric acid (*Z. Elektrochem.*, 1906, **12**, 173), concluded from potential measurements that the molybdenum was first completely reduced to the quinquevalent condition and that further reduction produced tervalent molybdenum without the intermediate formation of quadrivalent compounds. Depending on the concentration of the hydrochloric acid, the colour of the solution containing tervalent molybdenum could be either orange-red or green. The green colour was only obtained when the concentration of acid was less than 7*N*. In acid of higher concentration, the green stage was not reached and the colour of the tervalent molybdenum solutions was orange-red. Moreover, the production of the green colour was accompanied by a considerable fall of potential, although the alteration in permanganate titre was very small. This is in accord with the powerful reducing properties of the green solutions. They are extremely sensitive to air oxidation and immediately on exposure to air recover the orange-red colour. Chilesotti, with a certain amount of reserve, suggested that the appearance of the green colour might be due to the formation of small masses of molybdenum dichloride which had not been detected chemically, and that in the orange-red solutions bivalent molybdenum was not produced. The existence of two differently coloured solutions of chromic chloride is well known. Peligot (*Compt. rend.*, 1844, **19**, 783; *Ann. Chim. Phys.*, 1844, **12**, 537) first succeeded in obtaining green crystals of chromium trichloride, $[\text{Cr}(\text{H}_2\text{O})_4(\text{Cl}_2)\text{Cl}]\cdot 2\text{H}_2\text{O}$, by treating the insoluble violet anhydrous chloride with water in the presence of a small quantity of chromium dichloride.

"It is therefore possible," states Chilesotti, "that traces of molybdenum dichloride formed at the end of the reduction would favour the transformation of the molybdenum trichloride to the green form, which, on disappearance of the dichloride, would revert to the orange-red isomer."

It was thought, therefore, that it might be of interest to investigate the reactions of sulphur dioxide with the lower molybdenum compounds in view of the possible stages of oxidation and also to determine whether there was any distinctive difference in the reactivity of the green and orange-red solutions with this gas. In connexion with Chilesotti's hypothesis, it is worthy of note

that whilst cuprous chloride, stannous chloride, or other reducing agents (Rohland, *Z. anorg. Chem.*, 1899, **21**, 37; Drucker, *Z. physikal. Chem.*, 1901, **36**, 173) have the power of causing solution of the insoluble chromium chloride, they are ineffective in the case of the anhydrous molybdenum trichloride.

Reference to the literature showed that the stage to which solutions of molybdic anhydride are reduced has been the subject of considerable investigation. Wernke (*Z. anal. Chem.*, 1875, **14**, 1) carried the reduction with zinc and sulphuric acid approximately to the condition $\text{Mo}_{12}\text{O}_{19}$. Dudley (*J. Amer. Chem. Soc.*, 1893, **15**, 519), using Jones's reductor, obtained slightly different results. Doolittle and Eveson (*ibid.*, 1894, **16**, 234), and Jones (*Amer. Inst. Min. Eng.*, 1889, **90**, 18, 705) obtained results similar to those of Wernke. Blair and Whitfield (*J. Amer. Chem. Soc.*, 1895, **17**, 747) and Millar and Frank (*ibid.*, 1903, **25**, 919) reduced the anhydride approximately to the stage $\text{Mo}_{24}\text{O}_{37}$. Noyes and Frohman (*J. Amer. Chem. Soc.*, 1894, **16**, 553), by replacing air with carbon dioxide, effected a reduction corresponding to Mo_2O_3 . Randall (*Amer. J. Sci.*, 1907, [iv], **24**, 313), using ferric alum in the reducing flask and decolorising with phosphoric acid according to Reinhardt (*Chem. Ztg.*, 1889, **13**, 323), obtained reduction to Mo_2O_3 . Scott (*J. Ind. Eng. Chem.*, 1920, **12**, 575), using a rotating zinc reductor, showed that the reduction reached the Mo_2O_3 stage. There seems little doubt, therefore, that under favourable conditions molybdic anhydride is reduced by zinc and sulphuric acid to the tervalent condition. The only reference to any lower stage being reached is an early investigation by von der Pfordten (*Annalen*, 1884, **222**, 155) in which possible reduction to Mo_3O_4 is mentioned.

Although Chilesotti carried out his detailed potential measurements in the presence of hydrochloric acid in the case of the green and orange-red solutions, he mentions that sulphuric acid solutions give analogous results. We have therefore carried out our experiments in the presence of this acid, as at fairly high temperatures the concentration of sulphuric acid solutions is more easily controlled than the concentration of hydrogen chloride solutions.

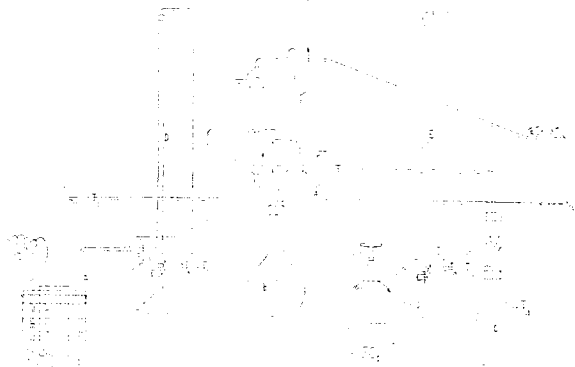
EXPERIMENTAL.

For the investigation of the reaction between sulphur dioxide and reduced solutions of molybdic anhydride in sulphuric acid, the apparatus shown in Fig. 1 was finally adopted.

The reduction of the solution was accomplished electrolytically in the cell A. This consisted of an outer glass vessel, which was used as the cathode chamber and was closed with a large rubber

bung. Through a hole in the centre of this passed a porous pot which served as the anode chamber. The electrodes were of smooth platinum, and the voltage was varied according to the concentration of the sulphuric acid, but was usually adjusted to give a current of 7–8 amperes. The cathode and the anode chambers were filled with the solution of ammonium molybdate and sulphuric acid. To prevent its temperature rising, the cell was immersed in a bath through which cold water continuously circulated. During the reduction, a stream of nitrogen was passed through the solution by means of the tube, *a*, in the cathode chamber. By suitably adjusting the taps, all air could be cleared from the apparatus. When the solution was completely reduced,

FIG. 1.



portions were forced into the burette, *D*, for analysis, whilst the remainder was transferred to the flask, *B*. The latter was provided with a double-surface condenser to minimise evaporation during the experiment. With taps 5 and 7 closed and 6 open, a stream of sulphur dioxide was passed through the reduced solution for half an hour at room temperature and then for twelve to fifteen hours with the temperature of the water-bath surrounding the flask kept constant at 90°.

Description of the Phenomena.

The colour of the completely reduced solution depended on the concentration of the acid present. In highly concentrated acid, the solution was salmon-pink, whereas with less concentrated acid it was either olive-green or bright green. On passage of sulphur

dioxide into the salmon-pink solution, the colour changed immediately to reddish-brown and then to carmine-red. If the solution was initially bright green, it became successively olive-green, brown, and carmine-red, whilst the olive-green solution became brown and finally carmine-red. The colour changes were accompanied by an opalescence, but on raising the solution to 90° the finely divided precipitate was coagulated. The colour of the solid thus produced varied from dark brown to light brown, according as the acid was concentrated or dilute. A deposit of sulphur gradually accumulated in the mouth of the flask and in the condenser. After the sulphur dioxide had passed for the required time, it was replaced by a current of nitrogen. The passage of this gas was continued until sulphur dioxide could no longer be detected at the exit tube. The solution, after cooling in the nitrogen stream, was forced through the glass-wool filter into the conical flask, *C*, by closing taps 8 and 10 and opening taps 9, 7, 11, and 15. By suitable rearrangement of taps, the red liquid was forced into the burette, *E*.

Quantitative Aspect of the Reaction.

The quantitative study of the reaction depends on a consideration of the nature of the initial and final solutions. In attempting to determine the stage of oxidation or reduction of a sulphuric acid molybdenum solution, it is necessary in the first place to know the total molybdenum content. Then since potassium permanganate solution will oxidise any reduced molybdenum solution to the sexavalent stage, one can readily deduce the exact constitution from a consideration of these two factors. After a detailed investigation of various methods for titrating reduced molybdenum solutions with standard potassium permanganate, we drew the conclusion that the best results were obtained when the fully reduced molybdenum solution was run directly into a stoppered flask containing ferric alum acidified with sulphuric acid and through which a current of nitrogen was passing. To determine the total molybdenum two methods were used. In the case of the initial solutions, these were boiled with hydrogen peroxide to effect oxidation to the sexavalent stage, and the molybdenum was precipitated as the trisulphide and weighed as the oxide in the usual way. This was done to determine whether the initial solution was reduced to the trivalent condition. Our experiments indicated that only when the solution was reduced to the stage developing the bright green colour, was reduction to the trivalent state complete.

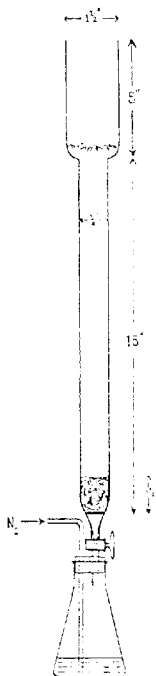
The total molybdenum in the final red solution was estimated

by means of the apparatus shown in Fig. 2, which is a modification of the Jones's reductor. Wedged in the bottom of the tube above the tap is a perforated disk which supports a glass-wool filter, $1\frac{1}{2}$ inches deep. The tube is then filled with small pieces of pure sheet zinc, bent into V-shape to prevent clogging as far as possible. Twenty c.c. of the red solution from burette *E* were used in each determination. In carrying out a determination, the reductor was

first cleaned with $2\frac{1}{2}$ per cent. sulphuric acid. The acid concentration of the red solution was adjusted to approximately 3*N*. It has been found advantageous to adjust the acid concentration to this normality, for if sufficient acid is not present, hydrolysis of the reduced molybdenum solution will occur, whilst if the acid is too concentrated, hydrogen sulphide will be formed, which will affect the permanganate titre. Ten c.c. of hot $2\frac{1}{2}$ per cent. sulphuric acid were introduced into the reductor and followed by the molybdenum solution, heated almost to boiling. The red solution was allowed to remain in the reductor until it was completely reduced to the green stage and then run directly into the flask containing ferrie alum solution, through which nitrogen continuously passed. Any molybdenum remaining in the reductor was removed by successive washings with hot $2\frac{1}{2}$ per cent. sulphuric acid. The contents of the flask were then titrated with standard permanganate. Blank experiments were always carried out and the necessary adjustments made. The accuracy of the method, which has been established by other investigators, is confirmed by the following typical results: Found: weight of MoO_3 in a given sample (*a*) by the gravimetric method = 0.1318 gram, (*b*) by the reduction method = 0.1320 gram. The result in the case of the reductor method is calculated on the assumption that the reduced solution is tervalent, and this assumption appears to be justified. The stage of oxidation of the final red solution is given by the expression $6 - 3t_1/t_2$, where t_1 is the permanganate titre and t_2 the titration value of the same volume of the red solution after passing through the reductor.

Degree of Oxidation.—Approximately 500 c.c. of the solution after reduction in the cell were allowed to react with sulphur

FIG. 2.



dioxide for twelve to fifteen hours, the reaction flask being immersed in a bath kept constantly at 90°.

TABLE I.

Concentration of molybdenum solution = 0.25 gram of molybdic anhydride per 100 c.c.						
Normality of acid	2	2.75	4	7	10	15N
Oxidation stage Mo_2O_x , where $x =$	3.78	3.89	4.04	4.26	4.33	4.20
Concentration of molybdenum solution = 2.5 grams of molybdic anhydride per 100 c.c.						
Normality of acid	2	5	7	10N		
Oxidation stage Mo_2O_x , where $x =$	3.76	4.15	4.20	4.20		

The table clearly shows that the extent to which oxidation by sulphur dioxide occurs depends on the acid concentration. In acid of low concentration the stage where $x = 4$ is not reached, whilst in the more concentrated acid this stage is surpassed. However, in no case does the oxidation proceed to the quinquevalent condition. There is no evidence that the concentration of the molybdenum materially affects the degree of oxidation.

Composition of the Precipitate.—The solid which separated out in the reaction between sulphur dioxide and the tervalent molybdenum solution mentioned above consisted of an intimate mixture of sulphur and a molybdenum sulphide. The colour of the deposit varied from dark brown to light brown, according to the amount of sulphur present. Chloroform extracted a large proportion of sulphur and left a dark brown powder which was practically insoluble in concentrated hydrochloric acid, only slightly soluble in warm, yellow ammonium sulphide, and contained molybdenum and sulphur. After prolonged extraction of the powder with chloroform, analysis of the residue failed to give concordant results, probably owing to the difficulty of completely extracting occluded sulphur. The residue was undoubtedly a sulphide of molybdenum, but not the trisulphide.

Degree of Oxidation in Dilute Acids.—Experiments were carried out with the tervalent molybdenum solutions in normal acid, and although the reaction with sulphur dioxide was apparently identical with that in acid of higher concentration, the results indicated the operation of some disturbing factor. The equilibrium values obtained under similar conditions varied considerably in different experiments, and were not of the order one would have expected from a consideration of the results given in Table I. When the acid concentration was reduced to semi-normal, a quite different phenomenon was exhibited on passage of the sulphur dioxide. A large part of the molybdenum was precipitated during the

experiment as a black mud, which behaved chemically as a molybdenum hydroxide, and is probably a mixture of $\text{MoO}_2 \cdot \text{H}_2\text{O}$ and $\text{Mo}(\text{OH})_3$. The final solution had a pale yellow colour, and although containing practically no molybdenum, it had an appreciable permanganate titre, the end-point being very indefinite. Only after long and vigorous boiling was the solution decomposed with deposition of sulphur. On boiling with dilute sulphuric acid, relatively large quantities of hydrogen sulphide were evolved. By addition of alkali, a small, greenish-brown precipitate was obtained, readily soluble in hydrochloric acid to a pinkish-brown solution, which on reduction with zinc acquired an olive-green colour. Apparently the solution contained thionic acids with a small quantity of molybdenum.

*Reaction of Hydrogen Sulphide with Tervalent
Molybdenum Solutions.*

The reaction of hydrogen sulphide with trivalent molybdenum solutions receives mention in Miller's "Inorganic Chemistry," 1878, p. 714, which states "hydrogen sulphide slowly produces a brown precipitate of hydrated sulphide, soluble in ammoniacal sulphide." Beyond this, no further information seems available. Our own experiments show that hydrogen sulphide may be passed through a green trivalent molybdenum solution for two or three hours without producing any effect, but if this saturated solution be sealed in a flask, a black precipitate will separate in the course of a few days. Qualitative tests on the precipitated sulphide indicate that it is identical in its chemical reactions with the brown sulphide obtained in our oxidation experiments. Quantitative analyses indicate that it is a sesquisulphide of molybdenum with varying water content.

Reaction of Sulphur with Tervalent Molybdenum Solutions.

The green trivalent molybdenum solution was allowed to react with finely powdered, recrystallised sulphur in a flask through which a current of carbon dioxide was passing. Hydrogen sulphide was slowly evolved at the ordinary temperature and the green solution gradually turned brown. On immersing the flask in a bath of boiling water, hydrogen sulphide was evolved in considerable quantity, the solution eventually turning red. This reaction is of interest as showing the powerful reducing properties of the green solution. No sulphide was precipitated in these experiments. Quadrivalent molybdenum solutions were not reactive with sulphur.

*Reactions of Acidified Tervalent Molybdenum Solutions with
Sodium Tetrathionate and Sodium Trithionate.*

Reference to recent literature on the stability of the polythionic acids gives many conflicting opinions. Riesenfeld and Feld (*Z. anorg. Chem.*, 1921, **119**, 225) state that in the presence of acid, of the three polythionic acids, tetrathionic acid is the least stable and decomposes relatively quickly into tri- and penta-thionic acids. Trithionic acid decomposes more slowly with formation of sulphur dioxide, whilst pentathionic acid decomposes only in the course of months, with separation of sulphur. Foerster and Hornig (*Z. anorg. Chem.*, 1922, **125**, 86) state that, of the polythionic acids and their salts, the tetrathionates are the most stable, the trithionates the most unstable, whilst the pentathionates occupy a mean position. Moreover, they state that a high concentration of hydrogen-ion retards the decomposition of tetra- and penta-thionic acids, but not of trithionic acid. These facts are of especial interest, for it has already been stated that when sulphur dioxide reacts in dilute acid molybdenum solutions, there seems good reason to suppose that a formation of thionic acids occurs and that the solution is comparatively stable. We considered, therefore, that the interaction of sodium tetrathionate and the reduced molybdenum solution might indicate whether our hypothesis was justified.

Sodium tetrathionate was placed in the reaction flask and a tervalent molybdenum solution in 3*N*-sulphuric acid run in, when hydrogen sulphide was immediately evolved in the cold. The reaction was allowed to proceed for twenty-one hours in a current of nitrogen, which expelled the hydrogen sulphide as it was formed. A brown precipitate formed, insoluble in hydrochloric acid and only slowly dissolved by yellow ammonium sulphide. The precipitate was not the outcome of reaction between the hydrogen sulphide and the green solution, for it has already been shown that a precipitate is only formed by saturating the solution with hydrogen sulphide and keeping it for a considerable time. Sodium tetrathionate treated with 3*N*-sulphuric acid is not reactive in the cold. Hydrogen sulphide is only evolved on vigorous boiling. The precipitated sulphide, therefore, appears to be a decomposition product of the initially formed molybdenum tetrathionate. The hydrogen sulphide evolved may have been due to the decomposition of this unstable tetrathionate or to the reduction of free tetrathionic acid by the tervalent molybdenum solution. It will also have been formed by the action of liberated sulphur on the green solution. It seems quite conceivable, therefore, that when sulphur dioxide is passed into the reduced molybdenum solution

an initial reduction to tetrathionic acid occurs. Such a hypothesis can account for the abnormal results obtained in dilute acid and for the production of a mixture of molybdenum sulphide and sulphur in the more concentrated acids.

Sodium trithionate reacts similarly with the tervalent molybdenum solution. However, experiments with trithionic and tetrathionic acids have led us to the conclusion that tetrathionic acid is the more stable and we incline, therefore, to the view that the initial reduction product of the sulphur dioxide is tetrathionic acid.

The Reducing Action of Sulphur Dioxide.

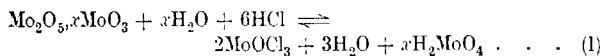
One of the characteristic tests for molybdenum is the production of a blue colour when sulphur dioxide or hydrogen sulphide is passed into an acid solution containing sexavalent molybdenum. This coloration is due to the formation of molybdenum-blue, an oxide of the form $\text{Mo}_2\text{O}_5 \cdot x\text{MoO}_3$. If, however, sufficient acid is present, no such reduction will be effected. Edgar (*Amer. J. Sci.*, 1908, [iv], 25, 332) proposed to estimate vanadium in the presence of molybdenum by boiling the solution with sulphur dioxide in the presence of definite concentrations of sulphuric acid, whereby the vanadium would be reduced but the sexavalent molybdenum would be unaffected. In our experiments, a solution containing 2.5 grams of molybdic anhydride per litre of 2.5*N*-sulphuric acid gave a faint blue colour on treatment with sulphur dioxide for eight hours at 90°, but with higher concentration of acid no reduction was noted. Evidently reduction of sexavalent molybdenum solutions can be inhibited by the presence of sufficient sulphuric acid, the normality of which will depend on the concentration of molybdic anhydride present.

We then investigated the reaction of sulphur dioxide with solutions of molybdenum corresponding to stages of oxidation slightly higher and slightly lower than the quinquevalent condition. The following table presents a few typical results obtained with solutions containing 3 grams of molybdic anhydride per litre of sulphuric acid of definite acidity, which were reduced electrolytically to definite stages and treated at 90° with a slow stream of sulphur dioxide. Ten c.c. of solution were used for each titration.

TABLE II.

Normality of sulphuric acid.	C.c. of KMnO_4 required for Mo^{V} .	C.c. of KMnO_4 .		Time in hours.	Remarks.
		Initial value.	Final value.		
1	2.1	1.9	1.9	12½	Molybdenum-blue formed
1	2.1	1.9	1.9	24½	"
1	2.1	2.15	2.15	24	No change
3	3.8	4.30	4.30	40	"

The above table clearly shows that solutions containing molybdenum in the quinquevalent condition were unaffected by the passage of sulphur dioxide, whereas those with molybdenum corresponding to a slightly higher stage of oxidation gave rise to molybdenum-blue. As the titrations did not vary before and after the reaction with sulphur dioxide, and as no sulphur was produced, it did not appear that oxidation had taken place. Solutions of the same concentration and titre as the first two solutions mentioned above were heated for a long period in a current of nitrogen, and it was found that they also gave rise to molybdenum-blue, proving that the sulphur dioxide had no specific effect on the reaction. Undoubtedly the formation of molybdenum-blue in all cases was the outcome of the equilibrium which has been established for hydrochloric and sulphuric acid solutions containing molybdenum in the quinque- and sexa-valent conditions:



In solutions corresponding to a stage just above the quinquevalent, sexavalent and quinquevalent molybdenum are present, and in accord with the above equilibrium they will form molybdenum-blue in greater or smaller amount, depending on the acid concentration. Molybdenum-blue is insoluble in 34 per cent. sulphuric acid, but in 56 per cent. acid it dissolves, giving rise to a yellow solution, whilst with 85 per cent. acid a green solution is obtained. In acid of high concentration we have found that yellow and green solutions are produced when sulphur dioxide reacts at 90° with molybdenum solutions at a slightly higher stage of oxidation than the quinquevalent. These effects are produced not by a specific action of the sulphur dioxide, but by the establishment of the above equilibrium relationship (see Abegg, "Anorganische Chemie," IV, p. 627).

In solutions representing a stage of oxidation below the quinquevalent stage, but greater than the maximum oxidation stage reached by reaction of the sulphur dioxide with tervalent molybdenum, namely, $\text{Mo}_2\text{O}_4 \cdot 2$, no reaction with the sulphur dioxide was observed.

Discussion of Results.

A consideration of the titrations and the reactivity of the green and red solutions has led us to the conclusion that only when the vivid green colour is obtained in the reduction of acid molybdenum solutions is the tervalent stage attained. Moreover, on oxidation, this vivid green colour reverts to an olive-green, brown, and then red, as shown by the reactions with sulphur dioxide and air. It

seems, therefore, that the red solution mentioned by Chilesotti is not in the tervalent condition.

From the results of the investigation, two facts stand out prominently. First, the degree of oxidation by sulphur dioxide of a tervalent molybdenum solution is dependent on the acid concentration. Secondly, under the most favourable conditions of acidity, the oxidation only proceeds to a stage represented approximately as $\text{Mo}_2\text{O}_{4.2}$. Chilesotti (*loc. cit.*) has shown in connexion with the molybdenum chlorides that in the reduction from the sexavalent stage the only distinct stages shown are those of the quinquevalent and tervalent compounds. It seems justifiable to assume that the sulphates will in all probability follow a similar course and on this conception the stage $\text{Mo}_2\text{O}_{4.2}$ is the result of the presence in the solution of certain proportions of tervalent and quinquevalent molybdenum. Moreover, the limited oxidation of tervalent molybdenum seems to point to the possibility of an equilibrium being established between the sulphates corresponding to these two stages. Although in the oxidation process precipitation of molybdenum sulphide occurs in addition to sulphur, the equilibrium reaction would be best expressed by the equation : $\text{Mo}_2(\text{SO}_4)_3 + \text{SO}_2 + 2\text{H}_2\text{SO}_4 \rightleftharpoons \text{Mo}_2(\text{SO}_4)_5 + \text{S} + 2\text{H}_2\text{O}$. . (2) Such an equation indicates the favourable influence of acid concentration on the degree of oxidation. On the other hand, neither sulphur nor sulphur dioxide has been shown to reduce molybdenum sulphate solutions corresponding to a degree of oxidation greater than $\text{Mo}_2\text{O}_{4.2}$ and less than the quinquevalent stage. This phenomenon is entirely analogous to that exhibited by the iron phosphates in their reactions with sulphur dioxide (F., 1920, 117, 1241), and an explanation similar to that given there seems applicable to the present case. Undoubtedly the non-reducibility of molybdenum sulphates, whether in the sexavalent condition in the presence of sufficiently concentrated acid or between the stages of oxidation represented by $\text{Mo}_2\text{O}_{4.2}$ and Mo_2O_5 , is due to the presence of stable complexes which on ionisation give rise to complex anions containing the molybdenum. Nevertheless, it is quite conceivable that at the moment of its formation by oxidation of the tervalent molybdenum with sulphur dioxide, the quinquevalent molybdenum sulphate, before being taken up in the form of a complex, may be reactive with the finely divided sulphur or the sulphur dioxide, the equilibrium relationship being thereby established.

In dealing with molybdenum sulphate solutions containing molybdenum corresponding to stages between Mo_2O_5 and MoO_3 , the action of the sulphur dioxide is not specific, as such solutions form molybdenum-blue in accord with equation (1).

Summary.

1. Sulphur dioxide oxidises solutions of tervalent molybdenum in sulphuric acid to stages intermediate between the ter- and quinque-valent conditions, sulphur and a molybdenum sulphide being precipitated.

2. The degree of oxidation increases with increasing acid concentration, the maximum oxidation stage being approximately $\text{Mo}_2\text{O}_{4.2}$.

3. Sulphur dioxide does not reduce sulphuric acid solutions of molybdenum corresponding to stages between $\text{Mo}_2\text{O}_{4.2}$ and Mo_2O_6 .

4. Sulphuric acid solutions of molybdenum corresponding to stages slightly greater than Mo_2O_5 , when treated with sulphur dioxide, give rise to molybdenum-blue. This result is not a specific effect of the sulphur dioxide, but the realisation of the equilibrium shown in equation (1).

5. The reduction of molybdenum in the sexavalent condition by sulphur dioxide is inhibited by the presence of sufficiently concentrated sulphuric acid.

6. Tervalent molybdenum solutions in semi-normal sulphuric acid react differently with sulphur dioxide, tetrathionic acid probably being produced.

7. A simplified reductor method for the estimation of molybdenum is described.

In conclusion, we wish to express our thanks to the Department of Scientific and Industrial Research for a grant to one of us (N. D. S.) which has enabled this investigation to be carried out, and to the Chemical Society for a grant towards the purchase of some of the materials.

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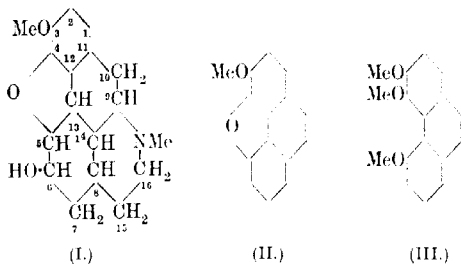
[Received, February 22nd, 1923.]

CXII.—*The Morphine Group. Part I. A Discussion of the Constitutional Problem.*

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LARGELY on account of the migration phenomena encountered in the study of this group of alkaloids, the morphine puzzle has absorbed the interest of many chemists in two generations, and in the case of no other natural product have so many different constitutional formulae been proposed or such a volume of experimental work, directed to the elucidation of constitution, recorded. It is therefore only because the present authors are convinced that insufficient attention has been paid to certain aspects of the

subject that they venture to advance still another suggestion. The present communication is intended to be the introduction to a series of experimental investigations, and is explanatory of a working hypothesis which we have adopted as the result of a review of the whole subject.



In order to provide a basis for discussion, formula (I) may be assumed to represent a possibly hypothetical dihydrocodeine, and the various structural elements in this expression call for brief examination. The phenanthrene skeleton, the tertiary $-NMe-$ group attached to a chain of two atoms not included in the phenanthrene nucleus, the aromatic character of the upper benzene nucleus, the position of the alcoholic hydroxyl and methoxyl groups, and the existence of an ether-bridge have all been proved at some stage or other of the work of Vongerichten, Knorr, Pschorr, Freund, and others. There is, however, an element of ambiguity in regard to all other points involved, although we believe that the case for the assumption that (I) is derived from codeine by the addition of two hydrogen atoms is an almost unanswerable one. The first question is the position of the oxygen bridge, and the arguments which can be used to support the usual view expressed in formula (I) are the following :

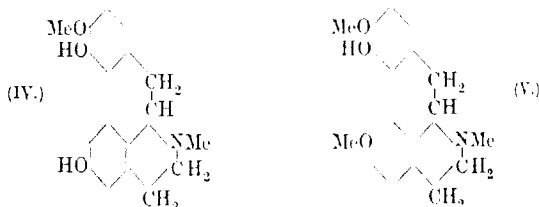
(1) Attachment of oxygen to 4* is certain, hence further attachment to 5 is the most natural assumption on stereochemical grounds. (2) Codeine may be degraded to methylmorphinol (II) by simple processes and the constitution of morphinol is proved by its conversion on fusion with potassium hydroxide into 3 : 4 : 5-trihydroxy-phenanthrene, the trimethyl ether (III) of which has been synthesised by Pschorr.† (3) The stability of the oxide ring towards reducing

* Reference is made to the various positions, numbered as in formula (I) by means of simple numerals: for example, 6 instead of position 6 or "the carbon atom in position 6."

† A bibliography of relevant literature bearing directly on the morphine problem is appended.

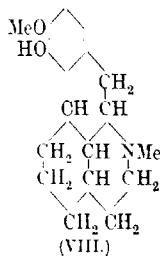
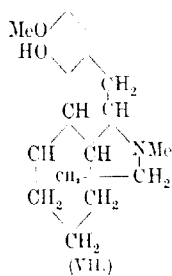
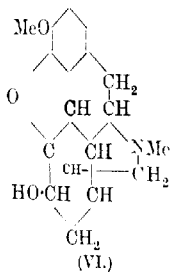
agents is very much diminished when a keto-group appears at 6 as in codeinone. This clearly indicates attachment of oxygen of the ether link to 5 or 7, and of these the latter presents no advantages whatever.

The attachment of the nitrogen atom to 9 follows from the results obtained by Knorr on the methine derived from hydroxy-codeine and by comparison with other alkaloids and phenanthrene bases (glaucine, bulboecapnine, dicentrine, laurotetanine, etc.) of proved and analogous constitution. The point of attachment of the 2-carbon chain, which, it may be remarked, cannot have the ethylidene arrangement $\text{-NMe}\cdot\text{CHMe}$, to the phenanthrene nucleus is the most controversial point included in the expression (f). Indeed in the greater number of morphine formulæ suggested in recent years the example of Knorr has been followed and 15 has been joined to 5. Nevertheless, the proof given by Pschorr of the constitution of *apomorphine* and of *morphothebaine* (IV) must be taken into account and in addition the relation of morphine, codeine, and thebaine to the bases which accompany them in the plant. In this connexion, particular attention may be directed to the alkaloid *isothebaine*, which has formula V, in which the only doubtful features are the positions assigned to the hydroxyl and methoxyl groups. This base occurs in the root of *Papaver orientale* after the period of blooming and withering of the aerial parts. During the time of vigorous growth of the plant, however, thebaine is the only alkaloidal constituent which can be isolated. It has been inferred that thebaine is actually converted into *isothebaine*, and as the latter substance is proved to belong to the aromatic phenanthrene group and to have a carbon atom of the side chain linked to 8, it is clear that thebaine should be similarly constituted.



For the above reasons, we consider it very probable that (f) represents codeine plus two hydrogen atoms and although, as has been indicated, this conclusion is by no means based on decisive experiments, it must be admitted that the assumption is in harmony with the broad lines of the chemistry of these alkaloids and is especially attractive if weight is attached to the argument connected

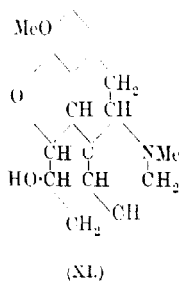
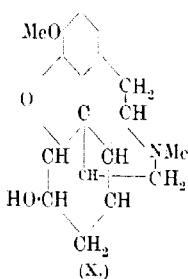
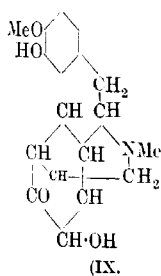
with their natural occurrence side by side with bases of proved isoquinoline structure. The chief reason why the fundamental basis afforded by this expression has been abandoned by many investigators is that it was supposed to be impossible to use it to develop a satisfactory formula for codeine, and it is the purpose of the present communication to remove this objection. The further problems which confront us are the determination of the manner in which the codeine formula is to be evolved from (I) by the removal of two hydrogen atoms, and the consistent explanation of the remarkable transformations which have been observed in this group with the aid of the expression so deduced. In the first place, it seems certain that codeine does not contain an ethylene linkage. The ultimate failure of the Pschorr formula was due to the fact that the morphine chemistry could not be explained on the basis of a structure derived from (I) and containing a double bond and even when the $\text{-CH}_2\text{-CH}_2\text{-NMe}$ chain is attached to 5 as in the Knorr formula there are grave disadvantages attached to every possible position for a double linking. These arise chiefly in regard to the relations of the isomeric methylmorphinethines, but the point need not be laboured, as there is positive evidence available that codeine contains an alicyclic bridge. Freund, Meibler, and Schlesinger have prepared two isomeric tetrahydrodeoxycodeines in regard to both of which the following statements are true. (1) The alcoholic hydroxyl is replaced by hydrogen. (2) Two hydrogen atoms are added at the oxygen bridge because these substances are phenolic in character. (3) These reduced deoxycodeines are tertiary bases, and therefore the C-NMe link is not broken. The α -form results when deoxycodeine (or α - or β -chlorodeide) is first reduced electrolytically at a lead cathode and the dihydrodeoxycodeine then treated with hydrogen in presence of palladium. The β -isomeride is obtained by the reduction of deoxycodeine hydrochloride by means of hydrogen in presence of palladium in aqueous solution.



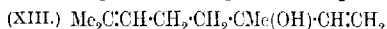
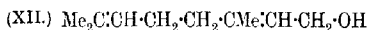
These results are with reason attributed by Freund and Speyer to the breaking of the bridge-ring system of codeine in two directions as shown in formulæ VI for codeine and VII and VIII for the isomeric tetrahydrodeoxycodeines. A second example of isomerism which must be due to the fission of the bridge-ring in two directions is dealt with in Part II of this investigation (p. 998). A further strong argument tending to prove the non-existence of a double bond in codeine is derived from the fact that the ketone codeinone can be obtained from the secondary alcohol codeine by oxidation with potassium permanganate in acetone solution. It is difficult to believe that this could be the case if codeine were unsaturated, and, moreover, in addition to codeinone, the chief product of the oxidation of codeine is a hydroxycodeine in which the new hydroxyl group occurs at 9 or 10, very probably 10, and for other reasons it is certain that the carbon atoms in these positions are saturated. Finally, in this connexion, it may be noted that the behaviour of thebaine towards ozone shows that this base, $C_{15}H_{21}O_3N$, is attacked by the reagent at one point only, since it is converted into an aldehyde or ketone, $C_{15}H_{21}O_5N$, termed *thebaizone*, which appears to be the methyl ester of a carboxylic acid. Thebaine is thus oxidised at the ethylene linkage or readily ruptured bridge which is produced in that enolic or other tautomeric form of codeinone of which the base is the methyl ether. In view of the close relation of thebaine to codeine, as proved by the hydrolysis of the former to codeinone and methyl alcohol, it may be inferred that what may be called the codeinoid unsaturation is of the polycyclic type. The researches of Freund on the oxidation of thebaine to hydroxycodeinone and on the attempted reduction of phenyldihydrothebaine lead to the same conclusion.

The next stage in our inquiry is to attempt a decision as to the position of the new ring which it is clearly necessary to introduce into the structure (I), and it is at this point that we wish to lay stress on a consideration to which, in our opinion, quite insufficient weight has been hitherto attached. Of the reactions encountered in the study of the chemistry of morphine and its allies none are more remarkable and surprising than those in which an aromatic phenanthrene system and an aminoethanol derivative are simultaneously produced. It is generally recognised that these degradations involve the break of a carbon-to-carbon union, and they occur in various types of morphine derivatives. It is not merely a case of a singular reaction occurring in one or two particular substances; the process is so common that its cause must be sought in some general property of the morphine structure. The driving force behind the change is doubtless the tendency to produce an aromatic nucleus, because the extrusion of the side-chain is never

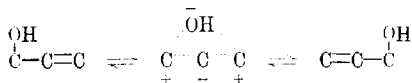
observed independently of the formation of the true phenanthrene derivative. But the obvious consequence has not previously been stated. *The formation of the aromatic phenanthrene derivative cannot take place for structural reasons unless the ethanamine side-chain is displaced in favour of a hydrogen atom or hydroxyl group.* Actually the displacement is normally in favour of a hydrogen atom. It is equally clear that the only structural condition which could inhibit aromatic ring formation is that the side-chain is attached to a quaternary carbon atom, one of those (13, 14) which are shared by two nuclei in the resulting phenanthrene derivative. An analogous case is that of abietic acid, which always loses a methyl group when it is converted into retene. The explanation in this example is accepted that the methyl group is attached to one of the carbon atoms common to two rings, but unaccountably the same deduction has not been drawn in relation to morphine and none of the current formulæ for the substance satisfies the above requirement. Applying it, we find that the bridge must be 8-15-13 or 8-15-14. It cannot be 8-15-5, because Knorr and Pechorr have observed degradative formation of phenanthrene derivatives in the case of methylthebainonemethine, and in this substance the oxide ring is broken and both 5 and 8 bear a hydrogen atom. If the bridge were 8-15-5, we should here have loss of the side chain without the alleged compelling reason and an explanation other than that now advanced would have to be found. That the position of the C-C-N chain presents an obstacle to the formation of a true aromatic ring follows also from the stability of hydroxythebainone. If this substance had the constitution (IX) assigned to it by its discoverers, it should pass into an aromatic compound such as morphothebaine (IV) with facility, and yet it is prepared from hydroxycodeinone by the action of a solution of stannous chloride in concentrated hydrochloric acid in a sealed tube at 100°. In agreement with these views, the alternative expressions for the constitution of codeine are X and XI and it will be convenient



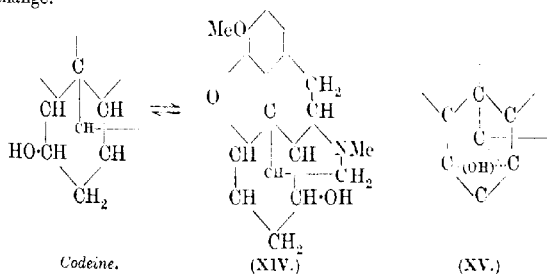
It is not known to which of the two series the various halogenomorphides and -codides belong. The tables show how often it is necessary to recognise the migration of hydroxyl from an α - to a γ -position and it will be noticed that the transformation can be reversed. In searching the literature for analogies, we encountered several cases of a very similar nature, and perhaps the best known of these concerns the relations of geraniol (XII) and linalool (XIII).



These alcohols are interconvertible in several ways. Linalool may be obtained from geraniol by heating with water at 200° under pressure, by hydrolysing the chlorides obtained from geraniol, and by passing steam into an aqueous solution of geranyl hydrogen phthalate. On the other hand, linalool may be converted into geraniol by hydrolysis of the products of the action of hydrochloric acid, by treatment with half a per cent. of sulphuric acid in acetic acid solution, and best of all by means of acetic anhydride, which produces geranyl acetate. The molecular changes involved in these reactions are illustrated in the scheme :



On the partial valency cycle theory of intramolecular re-arrangement this example belongs to the considerable group (including the Beckmann change) which involves a four-ring intermediate stage. The conversion of codeine into δ -codeine (XIV) can be quite analogously represented and the intermediate stage is given in the part-formula (XV) for purposes of comparison. It is a decided advantage of the bridge formulation of codeine (X) and the attachment of the bridge carbon to S that we are thus able to represent this characteristic wandering of oxygen as an interchange.



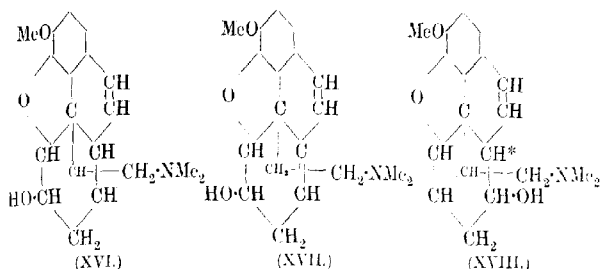
Both the codeine and ψ -codeine structures can be set up on models of the Engler type and are found to be relatively unstrained arrangements. On inspection, it is seen that the formation of *isocodeine* (6—OH series) from ψ -codeine through β -chlorocodide is most readily explicable if it is assumed that the hydroxyl and the bridge are in *trans*-relation in codeine. The argument of Knorr that codeine and ψ -codeine must have the same carbon skeleton because they may be converted into one and the same deoxycodine has little weight, since the deoxycodine is not obtained directly but through the halogeno-codides. Obviously a transformation of the more labile into the more stable series is not excluded and it would appear from this evidence that such a change does, in fact, occur during the formation as well as during the hydrolysis of the halogeno-codides.

The Isomeric Methylmorphimethines.

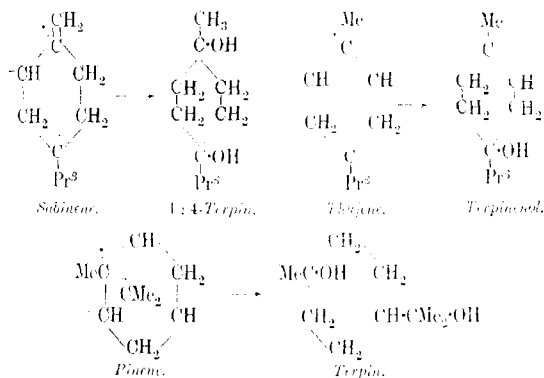
These substances are obtained by the decomposition of the codeine methohydroxides, and each of the codeines gives rise to a distinct methylmorphimethine. Those derived from codeine and *isocodeine* may be converted into isomerides by the action of alcoholic alkali and in other ways, whereas those derived from *allo-ψ*-codeine and ψ -codeine are not convertible into isomerides. It is very important to note that none of the methylmorphimethines can have more than one benzene ring because they are all unsaturated and the formula X is the first codeine formula to be proposed which offers an explanation of this fact. The occurrence of a second aromatic nucleus is, of course, inhibited by the attachment of the side chain to 13. The following table exhibits the relations and nomenclature of the six methylmorphimethines.

Methohydroxide from			
Codeine	<i>isocodeine</i>	<i>allo-ψ</i> -Codeine	ψ -Codeine
α	γ	ξ	ϵ
β	δ -Methylmorphimethine.		

It has been clearly proved that the hydroxyl group in α -, β -, γ - and δ -methylmorphimethines is at 6 and in the ϵ - and ξ -isomerides at 8. The codeine formula (X) allows the change of α into β and γ into δ to be explained in a simple manner as shown in the formulae XVI and XVII for the α - and β -isomerides, respectively.



α - and ζ -Methylmorphimethines receive the formula XVIII and the stability of these substances towards alcoholic potassium hydroxide is easily understood when it is considered that the more unstable bridge link is removed in this expression from the double bond and the tendency to form a conjugated system of two ethylene linkages has little scope. Examples culled from the terpene group show that a bridge breaks down with especial facility when in so doing it can directly produce a conjugated system. The formation of carvenone from carone, carvotanacetone from thujone, and eucarvone from carvone hydrobromide may be cited in this connexion. If, however, the bridge is connected to a carbon atom in the α -position with respect to a carbonyl or ethylene group, a conjugated system is not formed, because the α -carbon is negative and the β -atom positive. This point is illustrated in the schemes:

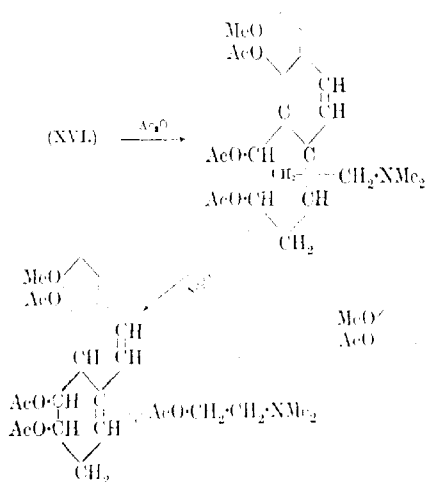


The case with which a double bond is formed in the conjugated position to an unsaturated group by a break away from the β -position and not from the α -position is analogous to the ready

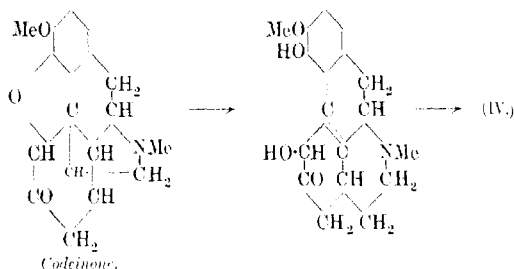
decomposition of hydraerylic acid and the stability of lactic acid. From the above it will be seen that in the α - and γ -methylmorphimethines we have the ideal conditions for the break of the bridged ring which is favoured both by the tendency to form a conjugated system and by the considerations connected with polarity. It may be remarked that we should expect ϵ -methylmorphimethine to be more stable towards acids than the ζ -isomeride, because in the former substance the hydroxyl group and the hydrogen atom marked with an asterisk in formula XVIII are in *trans*-relation. As a matter of fact, derivatives of *allo*- ψ -codeine have been little investigated.

The Degradation to Morphol Derivatives.

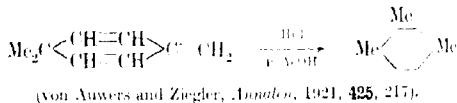
This fission takes place under a variety of conditions and the basic side chain is removed in various forms, which include dimethylaminoethanol and its acetate, dimethylaminoethyl ether, and tetramethylethylenediamine. The last substance results from the addition of dimethylamine to vinyl dimethylamine. A single example will suffice and the stages represented are, of course, hypothetical and designed to show that formula X provides a natural explanation. The point which is stressed is the compulsory removal of the ethylene side chain in order that the aromatic ring may be formed. A by-product of the reaction chosen is the acetyl derivative of β -methylmorphimethine.

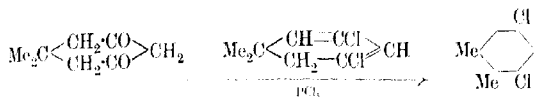


from chlorocodide, for example, is an entirely similar reaction. The former case may be chosen as an example :



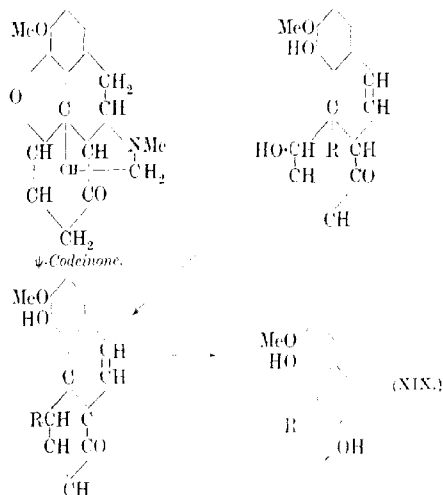
This base is formed by the action of hot dilute hydrochloric acid on thebaine, or the first product of its hydrolysis, namely, codeinone, and from ζ -codeinone by a similar method. It has been conclusively proved by Pschorr to have the formula XIX ($R = CH_2 \cdot CH_2 \cdot NHMe$) and therefore it is remarkable that it should be obtainable both from codeinone (CO at 6) and ζ -codeinone (CO at 8), especially since the reaction is facile in the former case and somewhat difficult to bring about in the latter. There are only two conceivable explanations whatever the constitution of morphine may be. Either oxygen wanders and this is very unusual in the case of oxygen of a carbonyl group, or the lower ring revolves about 180° at some stage. We take first the formation from ζ -codeinone in which the oxygen is already in the correct position. There are two ways in which blocked hydroaromatic substances having a suitable state of oxidation are known to pass into aromatic compounds. One is by displacement of a group from the molecule altogether and the other, almost as common, is by the wandering of a group to an adjacent carbon atom. We believe that the formation of thebenine involves such a migration and formula X for codeine leads to an explanation of the reaction for which there are many analogies. The following will serve to illustrate this point :





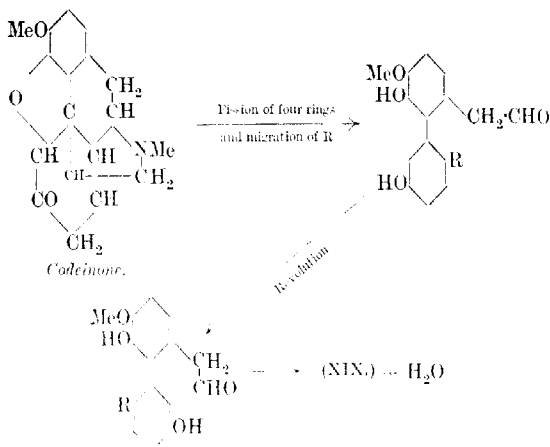
(Crossley and Le Sueur, T., 1902, **81**, 827, 1533).

The stages in the production of thebenine can be represented in the following manner ($\text{R} = \text{CH}_2\text{CH}_2\text{NHMe}$):



The molecular rearrangement is of the *isoborneol-camphene* type. Probably the difficulty experienced in the conversion of ψ -codeinone into thebenine is connected with the initial stages, because the bridge in the ψ -series is, in other reactions, more difficult to break than in the codeine series.

In the formation of thebenine from codeinone (thebaine) we may, of course, assume a similar mechanism plus migration of oxygen from 6 to 8 and in this respect formula X for codeine labours under no disadvantage from which other formulæ are free. The following mechanism seems, however, more probable and we put it forward with the reservation that the acceptance of this detail is not essential to our case.



If this is correct, the two schemes given are related in that the group R prefers to migrate to that adjacent carbon atom which is most remote from the carbonyl group. A careful examination of the whole of the literature relating to morphine and its allies has not disclosed any facts which are not in harmony with formula X for codeine, nor any which demand a special explanation, as in the case of thebaine.

The problem of thebaine is considered in Part II. Having now reviewed the facts on the basis of formula X, it remains to consider whether the alternative XI is equally satisfactory as a summary of the relations of these alkaloids. In our opinion, this is not so, although the arguments are not of a decisive character. If XI represents the molecule of codeine, ψ -codeine would be a cyclopentane derivative and the difference in stability of the ring systems should be considerable, so that the reversibility of the codeine- ψ -codeine transformation presents a difficulty. The isomerisation of α - and γ -methylmorphine-thines would not receive a very natural explanation and there would be no apparent reason why the ϵ - and ζ -isomerides are unattacked by alcoholic potassium hydroxide. The formation of thebaine from codeinone would necessarily involve rotation of the lower ring, and from ψ -codeine it would involve rotation and wandering of oxygen as well. For these reasons, we propose formula X as being, in all probability, the best representation of the constitution of codeine. Thebaine is the methyl ether of a tautomeric form of codeinone and on the basis of the codeine constitution now brought forward several

alternatives call for consideration. It is hoped that the matter will be discussed in detail in a future communication, but it may be stated now that we regard thebaine as dehydrocodeine methyl ether, in the molecule of which the carbon atoms at 6 and 14 are directly connected by a bond. This conclusion has been drawn mainly as the result of a study of hydroxycodeinone, a base prepared by Freund by the oxidation of thebaine with hydrogen peroxide. The formulæ proposed hitherto as symbols of the behaviour of hydroxycodeinone and its derivatives have all contained the group $-\text{CH}(\text{OH})-\text{CO}-$ in spite of the fact that it reduces neither Fehling's solution nor ammoniacal silver nitrate and cannot be converted into an osazone. If the hydroxyl group is not situated in the α -position with respect to carbonyl, it is equally certain that hydroxycodeinone and hydroxydihydrocodeinone are not β -hydroxyketones, because they are very much too stable and exhibit no tendency to lose the elements of water. Similar arguments can be cited to show that the only tenable hypothesis is that this oxidation product of thebaine is 14-hydroxycodeinone and this leads to the unexpected and remarkable thebaine formula which has been indicated above. Inspection of the models shows that the arrangement is not particularly strained, although more so than in codeine, and that carbon atoms in the allicyclic portion of the molecule occur at seven of the corners of a cube. A further interesting point is that the benzene ring is constrained and most naturally assumes the boat-shaped configuration recently suggested by Sir William Bragg as the probable arrangement existing in the crystal molecules of aromatic compounds. Finally, it may be pointed out that the pinocane formula for morphine is in reality a modification of Pschorr's original "pyridine" formula, and although we refrain from using the fact as an argument, a proceeding which would be an inversion of the logical order of development, it could have been printed without any modification of the text in place of the Pschorr formula in the scheme developed by one of us to represent the genetic relationships of the isoquinoline group of the alkaloids. It is merely a question of the direction of elimination of one molecule of water so as to produce a bridge instead of a double bond. The experimental work on which we are engaged in connexion with this subject is designed to provide crucial tests of the suggestions now advanced and is greatly facilitated by a generous gift of material from Professor W. H. Perkin, to whom we tender our warmest thanks. In collaboration with Dr. C. F. van Duin, one of us is also attacking the problem of the constitution of neopine, a rare opium alkaloid discovered by T. and H. Smith, and investigated by Dobbie and Lauder. This base was known

only as a gum which yielded a crystalline hydrobromide and it was thought to be a hydroxycodine. Dr. van Duin has luckily succeeded in crystallising the substance and it is a new isomeride of codeine. We are greatly indebted to Messrs T. and H. Smith for a supply of this unique material and for the trouble which they have taken in preparing it in a state of purity.

Summary.

A new formula for codeine (morphine methyl ether) is suggested, the main stages in the argument being the following:

1. Codeine is not unsaturated but contains a bridged ring.
2. The position of the bridge is deduced from (a) degradation of morphine or codeine to apomorphine and of codeine or thebaine to morphothebaine, (b) the relation of the morphine group to other opium alkaloids, (c) the consideration that in the decompositions leading to non-nitrogenous^{*} aromatic phenanthrene derivatives the breaking of a carbon-to-carbon union occurs because the point of attachment of the ethanamine chain offers a structural obstacle to the formation of aromatic nuclei.
3. The formula so deduced provides a natural explanation of the codeine- ϵ -codeine transformation, the isomerisation of α - and γ -methylmorphimethines, the production of methylmorphol, morphenol, morphothebaine, etc., in the course of various degradations.
4. Thebaine is regarded as owing its production from codeinone and ϵ -codeinone to a molecular rearrangement analogous to that of isoborneol into camphene.
5. A conceivable alternative constitutional formula accommodating the condition mentioned in (2. c) is found to be not so satisfactory a summary of the chemistry of morphine and its derivatives as that which is adopted.

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The above is not a complete list of the publications dealing with the chemistry of morphine and related alkaloids.

UNITED COLLEGE,

THE UNIVERSITY, ST. ANDREWS. [Received, February 23rd, 1923.]

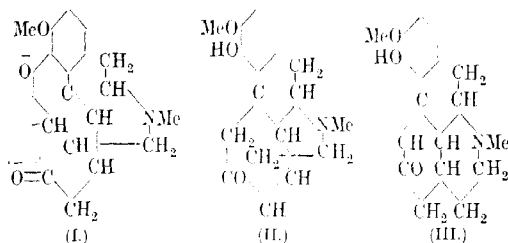
CXIII.—*The Morphine Group. Part II. Thebainone, Thebainol, and Dihydrothebainone.*

By JOHN MASSON GULLAND and ROBERT ROBINSON.

THEBAINONE is an isomeride of codeine which was first prepared by Pschorr, Pfaff, and Herrschmann (*Ber.*, 1905, **38**, 3160) by the reduction of thebaine by means of stannous chloride and hydrochloric acid at 100° and subsequently by Knorr (*ibid.*, 3174) by the application of a similar method to codeinone. It is derived from codeinone by the addition of two atoms of hydrogen, and the general character of the substance is readily deduced because the tertiary base is also a phenolic ketone, which has a pale yellow colour and dissolves in water to an intense yellow solution, whilst in alkalis it yields an orange solution. These properties recall the

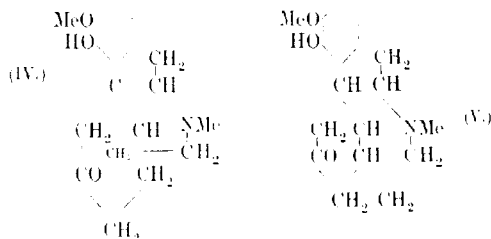
behaviour of salicylideneacetophenone and there can be little doubt that thebainone is an $\alpha\beta$ -unsaturated ketone.

Evidently the production of the substance from codeinone involves the opening of the oxide ring by reduction and simultaneously the bridged system is broken with formation of an ethylene linkage. On the basis of the formulae proposed in the preceding communication, codeinone (I) could undergo this transformation in two conceivable directions and thebainone might have either of the structures II and III. The \pm signs in the codeinone formula are intended to indicate an explanation of the reducibility of the oxide ring in this substance.



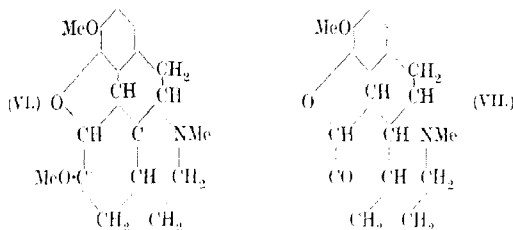
Knorr and Pscherr (*Ber.*, 1905, 38, 3172) have, however, shown that methylthebainonemethine may be degraded to dimethylmorphol, and consistently with the arguments advanced in Part I we must therefore prefer the constitution II, because III provides no explanation of the loss of the ethanamine chain in the course of the formation of the aromatic nucleus. When thebainone is reduced in aqueous solution by means of sodium amalgam, the orange colour of the liquid is gradually discharged and a dihydro-derivative is obtained. This substance was first prepared by Pscherr (*loc. cit.*) and regarded by him as the secondary alcohol corresponding to thebainene and hence named thebainol. It was crystallised from methyl alcohol and melted at 50–54°; the crystals contained solvent of crystallisation, but were dried before analysis. We have had no difficulty in preparing this product, but by crystallisation from dry ether have also obtained pure thebainol in colourless prisms melting at 135–136°. No proof of the secondary alcoholic character of thebainol was advanced by Pscherr, and the substance is in reality a ketone yielding a *semicarbazone* melting at 215–216°. Thebainol is therefore derived from thebainone by addition of two hydrogen atoms to the double bond and should have the constitution IV. An isomeride of thebainol has been prepared by Freund, Speyer, and Guttman (*Ber.*, 1920, 53, [B],

2250) and in a purer condition by Skita, Nord, Reichert, and Stukart (*Ber.*, 1921, 54, [B], 1560) by the reduction of thebaine in acetic acid solution by hydrogen in presence of palladium or platinum. This ketone melts at 137–138°, but it is levorotatory, whereas thebainol is dextrorotatory. Its semicarbazone melts at 225–226°, and a mixture with thebainol semicarbazone at about 205°. The two substances are quite distinct. The compound has unfortunately been called dihydrothebainone, although its relation to thebainone has never been proved in any way and in our opinion is non-existent. We propose, however, to retain for the present the misnomers thebainol and dihydrothebainone in order to avoid confusion, but at some later stage it may be desirable to replace the name thebainol by dihydrothebainol and dihydrothebainone by dihydro*iso*-thebainone. Dihydrothebainone is a tertiary basic, phenolic ketone. The phenolic hydroxyl must be at 4 and the carbonyl group at 6, so that the isomerism with thebainol can only be explained by the assumption that the bridged system has been broken down in each of the two conceivable directions and dihydrothebainone must have the constitution V. The possibility that thebainol and dihydrothebainone are stereoisomerides has not been overlooked, but the hypothesis does not appear to offer any consistent explanation of the facts.



This case of isomerism would be inexplicable if codeine contained one and thebaine two double bonds and the relation of thebainol to dihydrothebainone is quite analogous to that existing between the two tetrahydrodeoxycodines (Part I, p. 983). The former two substances are, in fact, 6-keto-derivatives of the latter two. In the reduction of thebaine to dihydrothebainone it has been shown that an intermediate product is a dihydrothebaine (m. p. 162–163°) which is not phenolic and in accordance with our view of the nature of dihydrothebainone and of thebaine is to be represented by the formula VI. This dihydrothebaine yields on hydrolysis a dihydrocodeinone (VII) crystallising in columns melting at 197–198° and

forming an oxime decomposing at 264° . Mannich and Löwenheim (*Arch. Pharm.*, 1920, 258, 295) have apparently obtained the same substance (prisms, m. p. $193-194^{\circ}$; oxime, m. p. 266°) by the reduction of codeinone with hydrogen in presence of palladium.



On further reduction by Clemmensen's method, this dihydrocodeinone yields a tetrahydrocodeinone the description of which by Mannich and Löwenheim does not quite coincide with that of either the α - or β -tetrahydrocodeinone by Freund, Melber, and Schlesinger (*J. pr. Chem.*, 1920, [ii], 101, 1). Clearly, a direct comparison would allow of the determination of the relation of the α - and β -isomerides to thebainol and dihydrothebainone and so provide interesting information in regard to the direction of scission of the ring system under various conditions. The structural distinction between thebainol and dihydrothebainone is further of interest in connexion with the constitution of codeinone.

Although it is usually assumed that the relation of codeinone to codeine is that of ketone to secondary alcohol, there is no satisfactory proof of this. Ach and Knorr (*Ber.*, 1903, 36, 3067), in the introduction to their paper, state that codeinone may be reduced to codeine, but no experimental details have been published and, as mentioned above, catalytic reduction produces a new ketone, dihydrocodeinone. Further it is stated in some text-books that codeinone undergoes the Claisen condensation and therefore must contain the group $-\text{CH}_2\text{C}(=\text{O})-$. But definite benzylidene and *is*onitroso-derivatives have only been obtained from ψ -codeinone, and our experiments have convinced us that codeinone, probably because of its instability in presence of acids or alkalis, does not yield similar compounds. The sole evidence that codeinone contains a reactive methylene group is furnished by the formation of azo-derivatives, but this is not decisive because the azo-compound might be of the form $\text{Ar-N}_2\text{-C}(=\text{O})-$ instead of $\text{Ar-N}_2\text{-CH-CO}$ or $\text{Ar-N}_2\text{-C}^-\text{C}(\text{OH})-$. In order to make this test a more stringent one, we have examined the behaviour of the azo-compounds on treatment with alkali. Comparison of a large number of cases shows

that if there is a mobile hydrogen atom in the *p*-nitrobenzeneazo-derivatives especially, as, for example, in those obtained by coupling with phenols or ketones containing the group $-\text{CH}_2\text{-CO}-$, an intense coloration is developed on the addition of potassium hydroxide to an alcoholic solution. No such colour is obtained by similar treatment of ethers of the nitrobenzeneazophenols or other *p*-nitrobenzeneazo-compounds not containing a mobile hydrogen atom in the system. The results show that codeinone forms azo-derivatives capable of passing into more intensely coloured modifications in presence of alcoholic potassium hydroxide and therefore the substance must contain the group $-\text{CH}_2\text{-CO}-$. Apart from these observations, the quite possible alternative is that codeinone is unsaturated and not related in a simple manner to codeine. But in that case codeinone would clearly have the same carbon skeleton as thebainone, into which it passes by reduction. We should thus have the following related series all having the same carbon skeleton: thebainol, thebainone, codeinone, dihydrocodeinone, dihydrothebaine, dihydrothebainone. If the view that thebainol and dihydrothebainone are structural isomerides is justified, it follows that codeinone cannot be an unsaturated ketone, but must contain the same alicyclic bridge as codeine. Inspection of the formula suggested for thebainone (II), thebainol (IV), and dihydrothebainone (V) shows that the first contains the group $-\text{CH}_2\text{-CO}-$ and the latter two the group $-\text{CH}_2\text{-CO-CH}_2-$. It appeared to be of great importance to confirm these deductions, because the occurrence of such a structure in both thebainol and dihydrothebainone would be inconsistent with a morphine formula in which the ethanamine chain is attached to 5, as in the Knorr formula or the dieyclic modification of this due to Freund and Speyer. Knorr and Hörlein (*Ber.*, 1907, **40**, 3349) state that Herrschmann (*Dissertation*, Berlin, 1906) had found that benzaldehyde condenses with thebainone, but no further publication has been made. We have now prepared and analysed benzylidenethebainone and piperonylidenebainone and a methylenedioxyquinoline derivative obtained by condensation of thebainone with 6-aminopiperonal (Rilliet and Kreitmann, *Helv. Chim. Acta*, 1921, **4**, 588). Piperonylidenebainone is an amorphous, pale yellow powder which exhibits the typical halochromy of a monopiperonylidene- $\alpha\beta$ -unsaturated ketone. It gives a reddish-purple solution in concentrated sulphuric acid closely resembling that given by benzylidenepiperonylideneacetone, but not so blue as the solution of dipiperonylideneacetone in sulphuric acid. The condensation of thebainol with piperonal in alcoholic solution containing sodium ethoxide was followed by observing the halochromy of the product. Apparently a monopiperonylidene

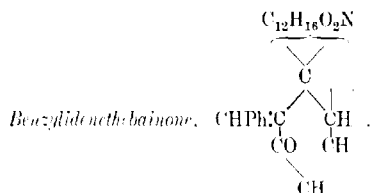
derivative was quickly produced and this gave a red colour in concentrated hydrochloric acid and thus resembled a monopiperonylidene saturated ketone. On prolonged treatment, the solution became bluer and ultimately a product was isolated, a yellow amorphous powder, which appears to be dipiperonylidene thebainol with $2\text{H}_2\text{O}$. This substance dissolves in hydrochloric acid to a pure blue solution which becomes green and then yellow on dilution with water. Dipiperonylidene thebainol methyl ether and dipiperonylidene dihydrothebainone methyl ether have also been prepared, but could not be crystallised. They exhibit the typical behaviour of dipiperonylidene-*cyclo*-ketones. The amorphous character of these substances is doubtless due to the fact that they are mixtures of stereoisomerides and it may be recalled that Haber has shown that the condensation of piperonal and acetone leads to both *cis*- and *trans*-piperonylideneacetones (*Ber.*, 1891, 24, 617). We are at present engaged in experiments designed to overcome this difficulty, but in the meantime there can be little doubt but that both thebainol and dihydrothebainone contain the group $-\text{CH}_2-\text{CO}-\text{CH}_2-$. If this is so, the ethanamine chain cannot be attached to 5 and thebenine must owe its formation from codeinone to molecular rearrangement as suggested in the preceding communication.

EXPERIMENTAL.

Note on the Preparation of Thebainone.

As mentioned by Pschorr (*loc. cit.*), exceedingly troublesome emulsions are formed during the extraction of the base with chloroform, and the following slight modification avoids this difficulty without affecting the yield. Thebaine, stannous chloride, and hydrochloric acid in the proportions recommended by Pschorr were placed in a wide bomb tube closed by a tightly fitting rubber stopper, kept in position by wires. This was immersed during twenty minutes in boiling water and at the end of this period rapidly cooled by the addition of cold water to the bath. The mixture was then added to 800 c.c. of water, well shaken, and treated with aqueous sodium hydroxide (10 per cent.) until a permanent milkiness was produced and the solution was very faintly acid to Congo-red. There is no difficulty in gauging this point, because the thebainone is itself an indicator, and if too much alkali has been added the colour changes from yellow to orange-red. Neutralisation was then completed by means of successive small amounts of sodium bicarbonate and the precipitate allowed to settle over-night. The clear orange solution was decanted, treated twice with animal charcoal, filtered, and extracted by gently shaking with chloroform. Two extractions

removed the whole of the thebainone, which was purified in the manner described by Pechorr.

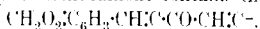


A solution of thebainone (1 gram), benzaldehyde (1.2 grams; 3 mols.), and potassium hydroxide (0.5 gram, dissolved in the minimum of water) in ethyl alcohol (10 c.c.) was boiled during two hours under reflux. The colour of the solution rapidly changed from light red to crimson. After the addition of water (100 c.c.), the liquid was just acidified with dilute hydrochloric acid and thoroughly extracted with ether in order to remove benzaldehyde. The orange-red solution was freed from ether by means of a current of air, neutralised by sodium carbonate, and the yellow precipitate collected, washed with water, and dried in a vacuum over sulphuric acid. The yield was 90 per cent. of that theoretically possible. The substance is very readily soluble in most organic solvents and could not be crystallised. It was purified by precipitation from benzene solution with light petroleum and obtained as a yellow powder which softened at 114° and melted at 120–123° (Found: C = 77.3; H = 6.8. $\text{C}_{25}\text{H}_{25}\text{O}_2\text{N}$ requires C = 77.5; H = 6.8 per cent.). The solutions of the substance in concentrated hydrochloric acid and sulphuric acid are deep red and become yellow on dilution with water. The picrate crystallises from alcohol in radiating clusters of short needles. It melts with decomposition at 194° after darkening at 191°. The methiodide crystallises from ethyl acetate in yellow, tubular columns which melt indefinitely, beginning at 195°.

Piperonylidene thebainone.

This substance was prepared in the same way as the benzylidene derivative, replacing the benzaldehyde by piperonal (1.6 grams). The bright yellow powder which separated on the addition of light petroleum to a benzene solution of the derivative softens at 118° and melts at 128–130° (Found: C = 72.4; H = 6.2. $\text{C}_{26}\text{H}_{25}\text{O}_3\text{N}$ requires C = 72.4; H = 5.8 per cent.). The solution in concentrated hydrochloric or sulphuric acid is intense reddish-purple and becomes pale yellow on dilution with water. Crystalline derivatives could

not be obtained. Piperonylidene thebainone was reduced in 5 per cent. acetic acid solution by means of hydrogen in presence of palladium. The colourless solution gave no coloration with concentrated hydrochloric acid, but still gave an orange solution on the addition of sodium hydroxide. The product was therefore in all probability homopiperonyl thebainone. The whole was rendered alkaline and reduced by means of sodium amalgam until the orange colour disappeared. The liquid was then just acidified with acetic acid, rendered alkaline by the addition of ammonia, and the colourless, sticky precipitate taken up in ether. After removal of the solvent, a colourless oil remained and this could not be crystallised. It gives coloured solutions neither in strong acids nor in dilute alkali, and is probably essentially homopiperonyl thebainol. On condensation with piperonal in the usual manner, a yellow product was obtained and this gave a deep red solution in concentrated hydrochloric or sulphuric acid and is probably piperonylidene homopiperonyl thebainol. The series of reactions confirms the view that piperonylidene thebainone contains the group



Dianhydro-6-aminopiperonal thebainone Dihydrobromide.

A solution of sodium ethoxide (0.5 gram Na) in alcohol (10 c.c.) was added to thebainone (1.1 grams) and 6-aminopiperonal (0.6 gram) dissolved in alcohol (10 c.c.), and the mixture boiled under reflux during six hours. The red solution was added to water (200 c.c.) and after filtration the phenolic base was precipitated by means of carbon dioxide. The yellow substance which separated dissolved as the passage of the gas was continued, but was redeposited on standing over-night exposed to the air. The precipitate was collected and dried (1.0 gram). All attempts to crystallise this quinoline derivative were unsuccessful, but a crystalline hydrobromide was obtained by the addition of concentrated hydrobromic acid to a solution of the base in a little acetic acid. The salt was crystallised from dilute aqueous hydrobromic acid and dried in a vacuum over sulphuric acid (Found: Br = 25.2; loss at 130° = 8.5. $\text{C}_{26}\text{H}_{21}\text{O}_4\text{N}_2 \cdot 2\text{HBr} \cdot 3\text{H}_2\text{O}$ requires Br = 24.9; H_2O = 8.4 per cent.). The glistening, orange-yellow, rectangular plates decompose at 258–260° and dissolve in sulphuric acid to a solution which exhibits bright emerald-green fluorescence.

Thebainol and its Semicarbazone.

This substance was prepared by the method of Pschorr (*loc. cit.*), which depends on the reduction of thebainone by means of sodium

amalgam. The product, crystallised from methyl alcohol, melted at 50—54°, but long standing of a 10 per cent. dry ethereal solution provided a small crop of colourless prisms which were used to seed an approximately 20 per cent. solution in the same solvent. The well-formed, rectangular prisms melted at 135—136° (Found: C = 71.6; H = 7.5. $C_{18}H_{23}O_3N$ requires C = 71.8; H = 7.6 per cent.). Thebainol is one of the few morphine derivatives which, like deoxycodine, are dextrorotatory. In ethyl alcohol, $c = 8.71$, $l = 0.5$ dem., $\alpha = +2.92^\circ$; whence $[\alpha]_D^{25} = +67.05^\circ$. In 5 per cent. acetic acid, $c = 2.368$, $l = 2.0$ dem., $\alpha = +1.58^\circ$; whence $[\alpha]_D^{25} = +33.07^\circ$.

On crystallisation of the product, m. p. 135—136°, from methyl alcohol, the melting point was again found to be 50—54°, but the substance resolidified and melted finally at about 135°. When the substance was mixed with dihydrothebainone (Freund, Speyer, and Guttmann's preparation), the melting point was depressed to 110°. Thebainol is readily soluble in dilute aqueous sodium hydroxide, but with a concentrated solution yields a precipitate of a colourless, crystalline sodium derivative.

Thebainolsemicarbazone was prepared in dilute acetic acid solution by the action of an excess of semicarbazide hydrochloride and sodium acetate. The mixture was warmed to 80°, then allowed to cool and, after five minutes, the solution was neutralised by sodium carbonate. The precipitate was collected and the derivative crystallised from aqueous alcohol and then from a mixture of ethyl alcohol and ethyl acetate. An identical product was obtained from pure thebainol, m. p. 135—136°, and from the original material having the properties recorded by Pschorr (Found: N = 15.8. $C_{19}H_{26}O_3N_4$ requires N = 15.6 per cent.). Rapid cooling of a solution in ethyl alcohol and ethyl acetate causes the separation of a cloud of globules which are so small that they may only be discerned under the higher powers of the microscope. Slow cooling produces frond-like bundles of slender needles and if crystallisation is very slow twinned prismatic needles are obtained. The substance melts at 215—216° as ordinarily prepared. After drying during four hours at 100° under 100 mm., there was no perceptible loss of weight, but the melting point rose to 217—218°. A mixture of thebainolsemicarbazone and dihydrothebainonesemicarbazone (m. p. 225—226°) melted at about 205°.

Thebainol Methiodide.—This derivative was obtained very readily by gently warming an alcoholic solution of thebainol and methyl iodide and allowing to remain during an hour. The addition of ether precipitated the substance in an amorphous condition and crystals were first obtained by the careful addition of ethyl acetate

to a solution in methyl alcohol. The crude product was then dissolved in methyl alcohol and addition of a crystal to the hot solution induced the crystallisation of most of the salt, which when pure is sparingly soluble in methyl alcohol. The substance was recrystallised from ethyl alcohol and obtained in colourless columns melting at 243° with decomposition [Found: I = 28.5, 28.9 (by titration). $C_{19}H_{26}O_3N$ requires I = 28.6 per cent.]. The salt is dextrorotatory in aqueous solution: $c = 2.061$, $l = 0.5$ dm., $\alpha = +0.48^{\circ}$; whence $[\alpha]_D^{25} = +46.56^{\circ}$.

Dihydrothebainonesemicarbazone.

In the preparation of dihydrothebainone from thebaine it was observed that the mother-liquors deposited a small crop of crystals which, after recrystallisation from alcohol, were colourless, prismatic tablets melting at 219° and at the same temperature when mixed with pure cryptopine. Evidently cryptopine occurs as an impurity in thebaine, but cannot be detected by the characteristic reaction with sulphuric acid because the colour is masked by the deep orange due to thebaine itself. The specimen of thebaine employed began to melt at 188° , whereas pure thebaine melts at 193° . On one occasion, the palladium catalyst was inefficient and the main product of the reduction was dihydrothebaine, m. p. 165° . The substance crystallised from methyl alcohol in rectangular prisms and was proved to be identical with the dihydrothebaine, m. p. $162-163^{\circ}$, of Freund, Speyer, and Guttmann (*loc. cit.*) because it yielded dihydrocodeinone, m. p. $197-198^{\circ}$, on hydrolysis with concentrated hydrochloric acid. *Dihydrothebainonesemicarbazone* was prepared in the manner prescribed above for thebainolsemicarbazone. It crystallises from aqueous alcohol in colourless, elongated prisms melting at $224-225^{\circ}$. The substance, dried in a vacuum over sulphuric acid, lost 9.6 per cent. at $110-115^{\circ}$ and then melted at $226-227^{\circ}$ (Found, in anhydrous substance: N = 15.7. $C_{19}H_{26}O_3N_2 \cdot 2H_2O$ requires $H_2O = 9.1$; $C_{19}H_{26}O_3N_2$ requires N = 15.6 per cent.).

Triphenylglycidyl etherthebainol.

A solution of thebainol (1 gram), piperonal (2 grams), and potassium hydroxide (0.5 gram) in ethyl alcohol (10 c.c.) was boiled under reflux. The yellow colour rapidly changed to red and a sample withdrawn after twenty minutes gave a bright red solution in concentrated hydrochloric acid. After two hours, the base was isolated exactly as described above in the case of benzyldienethebainone. The yellow powder gave a purple colour

with concentrated hydrochloric acid. It was noticed, however, that the initial treatment with dilute hydrochloric acid failed to dissolve a small quantity of brown material, which gave a bright blue colour with concentrated hydrochloric acid. It seemed probable, therefore, that thebainol condenses readily with one molecule of piperonal and forms a dipiperonylidene derivative with much greater difficulty. The product was accordingly dissolved in ethyl alcohol (10 c.c.) and, after the addition of piperonal (2 grams) and potassium hydroxide (0.5 gram, dissolved in a little water), the mixture was boiled during twenty hours. The colour in concentrated hydrochloric acid gradually changed from reddish-purple to pure blue and at the end of the period mentioned the dark red solution was added to water (150 c.c.) and carefully acidified with ice-cold dilute hydrochloric acid. The reddish-brown tar was collected on a glass rod, well washed with ether, and dissolved in acetic acid. On dilution with water, a precipitate was obtained and, after neutralisation of the acid present, this was collected, dried, and the substance purified by repeated precipitation from chloroform solution by means of light petroleum. The orange-yellow powder could not be crystallised and was dried in a vacuum over sulphuric acid (Found: C = 67.4; H = 6.0; N = 2.4. $C_{24}H_{31}O_7N \cdot 2H_2O$ requires C = 67.9; H = 5.8; N = 2.4 per cent.). The substance dissolved in concentrated sulphuric acid to a purple solution and in concentrated hydrochloric acid to a deep pure blue solution which became green and then pale greenish-yellow on dilution with water. The substance is readily soluble in acetone, chloroform, ethyl acetate, or alcohol, sparingly soluble in benzene, and almost insoluble in ether or light petroleum. The condensation of dihydrothebainone with piperonal was also carried out with similar results.

*Dipiperonylidene Derivatives of Thebainol Methyl Ether and
Dihydrothebainone Methyl Ether.*

Methylation of thebainol and dihydrothebainone was effected by means of diazomethane, which was prepared by the method of Werner (T., 1919, **115**, 1098) from nitrosomethylurea. The decanted ethereal solution of the reagent was found to be unsuitable for use in these examples and was distilled. Moreover, methylation did not proceed in ether alone and it was found necessary to add the solution of diazomethane (6 mols.) to a 10 per cent. solution of the phenolic base in pure ethyl alcohol. The use of isoamyl ether was not advantageous. After allowing to remain at the ordinary temperature during twenty-four hours, during which time bubbles of nitrogen were evolved, the solvent was removed by distillation

and the oily residue triturated with dilute sodium hydroxide to separate any unchanged material. The oil was then taken up in ether and the solution washed, dried, and evaporated. The pale yellow, viscid residue, consisting either of thebainol methyl ether or of dihydrothebainone methyl ether, could not be crystallised. Thebainol methyl ether exhibited a curious behaviour on standing. Although completely soluble in ether when first prepared, some process of auto-condensation or oxidation occurred and when treated with the solvent there was a flocculent residue. After evaporation of the filtered solution and allowing to remain for a further period, more of this insoluble material was produced; the process was repeated five times with the same result and apparently would proceed indefinitely. The average yield of the methyl ethers was 60 per cent. of that theoretically possible.

Methylthebainol methiodide was obtained by the addition of a little more than one molecular proportion of methyl iodide to a solution of the ether in ethyl acetate. The precipitated oil solidified on rubbing with ether and acetone, and the substance crystallised from methyl alcohol in irregular prisms which melted at about 245° with decomposition [Found, in material dried at 100° in a vacuum: $I = 27.8$ (by titration). $C_{20}H_{28}O_3NI$ requires $I = 27.8$ per cent.].

Methyldihydrothebainone methiodide separated in clusters of boat-shaped crystals when methyl iodide was added to a solution of the base in ethyl acetate. The derivative was recrystallised from methyl alcohol and obtained in diamond-shaped prisms which darkened slightly at $257-258^{\circ}$ [Found, in material dried at 100° in a vacuum: $I = 27.8, 27.7$ (by titration). $C_{20}H_{28}O_3NI$ requires $I = 27.8$ per cent.].

The condensation of thebainol methyl ether and of dihydrothebainone methyl ether with piperonal gave identical results. The base (1.6 grams) and piperonal (3.1 grams) were dissolved in ethyl alcohol (25 c.c.) and after the addition of a solution of sodium ethoxide (0.5 gram of sodium in 10 c.c. of alcohol) the mixture was boiled under reflux during twelve hours. A further quantity of piperonal (1.5 grams) was then added and the boiling continued during twelve hours. The dark red liquid was poured into moderately concentrated brine, and the reddish-brown precipitate collected, washed, and dried. After a preliminary purification by precipitation from a filtered chloroform solution by means of light petroleum, the yellow powder was dissolved in a large volume of hot alcohol, the solution treated with animal charcoal, filtered, and concentrated. The compound separated in microscopic, transparent, yellow globules and in a similar condition from ethyl acetate.

The derivative from methylthebainol softened at 149° and began to melt at 156° ; that from methyl-dihydrothebainone softened at 160° and began to melt at 166° . For analysis, the substances, which tend to retain water to a marked degree, were dried at 110° (Found: for dipiperonylidene-methylthebainol, $C = 71.2$, 71.5 ; $H = 5.5$, 5.7 ; for dipiperonylidene-methyl-dihydrothebainone, $C = 71.9$; $H = 6.1$; $N = 2.4$. $C_{35}H_{33}O_7N \cdot 0.5H_2O$ requires $C = 71.4$; $H = 5.8$; $N = 2.3$ per cent.). The colour reactions of the two compounds are identical. In sulphuric acid, a rich purple solution is produced, and addition of hydrochloric acid to a solution in glacial acetic acid develops an intense green coloration, which is also obtained from dipiperonylidene-tropinone under similar conditions.

Interaction of Bromocodeinone and Hydrogen Iodide.

A solution of bromocodeinone hydrobromide (0.1256 gram) in ethyl alcohol (20 c.c.) and water (20 c.c.) was freed from air by boiling and passing a current of carbon dioxide. Potassium iodide (1.0 gram) was then added, and after cooling to 40° air-free 2*N*. hydrochloric acid (10 c.c.) was introduced and the mixture maintained at 45° in the neutral atmosphere during three and a half hours. The free mineral acid in the cooled solution was neutralised by the addition of potassium acetate, and the iodine set free in the reaction required 10.2 c.c. of 0.0252*N*-sodium thio-sulphate. Hence one molecule of bromocodeinone hydrobromide liberates 0.97 atom of iodine. This is half the amount anticipated on the assumption that the process is a straightforward reduction to codeinone, but this substance, if formed, would be converted in the acid solution into thebenine to some extent and loss of halogen as the result of substitution in this phenol is a natural consequence. On the other hand, the reaction may follow an abnormal course such that one molecule of iodine is produced from two molecules of bromocodeinone. An experiment was carried out under the conditions described above but without bromocodeinone hydrobromide and no trace of iodine was liberated.

Coupling of Codeinone with Diazonium Salts.

The diazonium salt in aqueous solution in presence of excess of sodium acetate was added to an alcoholic solution of codeinone; subsequently alcoholic potassium hydroxide was introduced. Very dilute solutions were employed and under similar conditions codeine gave either no coloration or very pale shades unchanged in tone by the addition of alkali.

Base.	Colour produced.	After addition of KOH.
<i>p</i> -Toluidine	Yellow	Orange-red
<i>p</i> -Phenetidine	Yellow	Yellowish-brown
Cresidine	Yellow	Brownish-red
<i>o</i> -Nitroaniline	Yellow	Purplish-brown
<i>m</i> -Nitroaniline	Yellow	Reddish-brown
<i>p</i> -Nitroaniline	Orange-yellow	Reddish-violet
<i>p</i> -Nitro- <i>o</i> -toluidine	Yellow	Brownish-orange
Nitrocresidine	Brown	Brownish-violet
Picramic acid	Orange-yellow	Deep brown
2 : 4-Dinitro- <i>m</i> -toluidine	Lemon-yellow	Brownish-red tending to violet
<i>p</i> -Aminobenzoic acid	Pale yellow	Red
Aminosulphosalicylic acid	Greenish-yellow	Reddish-orange
Aminoazobenzene	Red	Dark brown
α -Naphthylamine	Orange-brown	Brownish-red
Naphthionic acid	Orange	Crimson
Tolidine	Orange-red	More intense
Dianisidine	Bluish-red	More intense
Diaminoveratrone	Orange-brown	Reddish-brown

Attempts to condense codeinone with benzaldehyde, anisaldehyde, piperonal, and nitrosodimethylaniline in the presence of various catalysts and under a variety of conditions were fruitless.

One of us (J. M. G.) desires to express his thanks to the Carnegie Trust for a scholarship which has enabled him to take part in this investigation.

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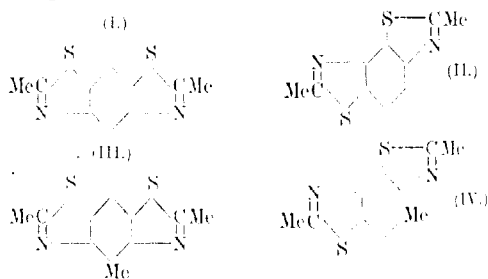
CXIV.—Benzbisthiazoles. Part III.

By STEPHEN RATHBONE HOLDEN EDGE.

THE result indicated by the work described in the two papers already published (T., 1922, 421, 772; this vol., p. 153), namely, that the main oxidation product of dithioacetyl-*m*-phenylenediamine in alkaline solution is 2 : 6-dimethylbenzbisthiazole (I), a symmetrical three-ring structure, rather than the unsymmetrical 2 : 7-dimethylbenzisobisthiazole (II), has been criticised because so many of the methods for making three-ring structures yield only the unsymmetrical form, or yield that form much more easily than the other. It is a well-known fact that when a β -side chain in a naphthalene molecule closes up to form a third ring it closes in the α -position, and that substitution in the α -position prevents the ring formation. Also in the synthesis of phenanthrolines from the phenylenediamines by the Skraup method, a synthesis having some analogy to the

method used in the present work, only the unsymmetrical forms are produced (Skraup and Vortmann, *Monatsh.*, 1882, **3**, 571; 1883, **4**, 574). Hence it seemed worth while to settle the point as to whether the method employed for making the benzbisthiazoles would yield a symmetrical three-ring structure easily or not. Pure 2:6-dinitrotoluene formed a convenient starting point. This was reduced and the resulting diamine acetylated. A diacetyl derivative having all the properties described by Green (T., 1891, **59**, 1017), especially the interesting sublimation near the melting point, was obtained. An error appears to have crept in concerning the melting point of this compound, as it was found to melt just 100° higher than the figure given in the above reference. The conversion of this diacetyl-2:6-diaminotoluene, through the corresponding dithioacetyl derivative, into 2:4:6-trimethylbenzobisthiazole (III) was accomplished with remarkable ease. The contrast between the ease of this preparation and the difficulty of the preparation of the unsymmetrical 2:4:7-trimethylbenzobisthiazole (IV) described in Part II is very marked. This bisthiazole, like the 2:6-dimethylbenzobisthiazole previously described, is strictly a monoacid base only. No evidence whatever of the existence of diacid salts, or a dimethiodide, was obtained. This fact completes the proof of the symmetrical structure of the previously prepared 2:6-dimethylbenzobisthiazole, and shows that in the case of this particular synthesis of a three-ring structure the symmetrical form is more easily produced than the unsymmetrical.

The way in which the power of the nitrogen atoms to become quinquivalent varies with the arrangement of the two thiazole rings in the molecule is receiving careful attention and will be referred to again in a later communication.



EXPERIMENTAL.

Diacetyl-2:6-tolylglucodiamine.—The method for preparing the diamine from 2:6-dinitrotoluene, as given by Ullmann (*Ber.*

(1884, 17, 1960), was modified in that, after precipitation of the tin, the solution was evaporated to dryness on a water-bath, and excess of concentrated caustic soda solution added. The diamine was precipitated as an oil, which solidified as a cake on the surface. It was removed, and the remaining alkaline solution extracted with ether. The whole yield was dissolved in ether, the ethereal solution dried with sodium sulphate, and the ether evaporated. The resulting solid diamine was acetylated directly with acetic anhydride. The reaction was vigorous, and, after adding excess of the anhydride, the mixture was poured into water, and the white, crystalline precipitate filtered off and dried. Yield = 24 grams from 40 grams of 2:6-dinitrotoluene. The melting point was found to be $302-303^{\circ}$ and to be unchanged after sublimation.

Dithioacetyl-2:6-tolylenediamine.—Following exactly the method as previously given, the crude thioacetyl derivative was obtained as a light brown powder. Yield = 38 grams. After several crystallisations from alcohol, the melting point became constant at 275° . No eutectic mixture of the di- and mono-thioacetyl derivatives was found in this case, nor was it found possible to isolate the monothioacetyl derivative (Found: S = 26.55; N = 12.11. $C_{11}H_{14}N_2S_2$ requires S = 26.90; N = 11.77 per cent.).

2:4:6-Trimethylbenzobisthiazole (III).—Fifteen grams of the crude dithioacetyl-2:6-tolylenediamine were dissolved in 750 c.c. of water containing 50.7 grams of caustic soda, and the mixture was poured into a solution of 100 grams of potassium ferrocyanide in 1050 c.c. of water. A precipitate of the bisthiazole formed almost immediately. After standing one day, this was filtered off. It was purified by dissolving in concentrated hydrochloric acid, diluting, filtering, and reprecipitating with caustic soda. The product crystallised readily from alcohol in dull pale yellow crystals, m. p. $185-186^{\circ}$. Yield = 6 grams. This compound can be distilled under reduced pressure with slight decomposition only; b. p. $280^{\circ}/40$ mm. (Found: S = 27.24; C = 56.56; H = 4.06. $C_{11}H_{10}N_2S_2$ requires S = 27.35; C = 56.41; H = 4.27 per cent.).

2:4:6-Trimethylbenzobisthiazole Methiodide. —On heating a weighed quantity of the bisthiazole in a sealed tube with excess of methyl iodide at 100° for a long time, the product was a viscous mass, containing crystalline matter, which increased in amount slowly on prolonged heating. The experiment was repeated, heating at 150° being continued for six hours. The product was entirely crystalline, consisting of small, brown, needle-like crystals. After leaving in a current of air until the weight became constant, the increase was found to be just less than that required for the monomethiodide. On crystallising from a small quantity of water,

or from rather more alcohol, nearly white, needle-shaped crystals resulted. These melt sharply at 211° if heated quickly, but begin to decompose and melt at $203\text{--}205^{\circ}$ if heated slowly (Found: I = 32.82. $\text{C}_{12}\text{H}_{13}\text{N}_2\text{IS}_2$ requires I = 32.78 per cent.).

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[Received, March 29th, 1923.]

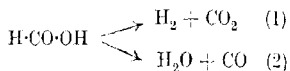
CXV.—*The Energy of Activation in Heterogeneous Gas Reactions with Relation to the Thermal Decomposition of Formic Acid Vapour.*

By CYRIL NORMAN HINSHELWOOD and BRYAN TOPLEY.

ONE of the most important quantities associated with a homogeneous chemical reaction is the heat of activation, which represents the energy required to enable a molecule to undergo chemical decomposition. When a molecule is adsorbed on the surface of a catalyst, its stability is modified by the forces between it and the surface so that a smaller amount of energy suffices to bring it into the reactive condition. This appears to be one of the principal factors involved in the action of heterogeneous catalysts. The energy of activation is connected with the temperature coefficient of the velocity constant by the equation $d \log k/dT = E/RT^2$. It is seldom possible to compare directly the heat of activation for the two cases of a gaseous reaction proceeding in the homogeneous phase and the same reaction catalysed by a surface. But the results of Trautz and Bhandarkar (*Z. anorg. Chem.*, 1919, **106**, 95) on the homogeneous decomposition of phosphine at high temperatures show that the heat of activation is considerably greater than that found for the heterogeneous decomposition on the walls of the vessel which predominates at lower temperatures. And in general it is recognised that heterogeneous reactions have smaller temperature coefficients than homogeneous reactions. This, however, is not an unequivocal result, since the amount of the reacting substance adsorbed on the surface of the catalyst, and therefore actually participating in the reaction, may diminish as the temperature rises. This would make the apparent value of E , calculated from the observed influence of temperature, smaller than the true value, which measures the actual stability of the adsorbed molecule. It appears from the approximate calculation given on p. 1022 that the apparent value is less than the true value by an amount which is approximately equal to the heat of adsorption of the reacting substance by the catalyst. Only if this is small can the

true heat of activation be found directly from the variation of reaction velocity with temperature.

The thermal decomposition of formic acid is a convenient reaction to study from the point of view of the connexion between heat of activation and velocity. The question may be approached in two ways. First, the relative ease with which the two alternative reactions



proceed on the same catalyst may be investigated, and, secondly, the individual reactions may be followed on a number of different catalytic surfaces. On glass surfaces, it was found (Hinshelwood, Hartley, and Topley, *Proc. Roy. Soc.*, 1922, [A], **100**, 575) that reaction (2) was associated with a heat of activation so much lower than that of the alternative reaction that it might have been expected to predominate entirely. Since both reactions may actually proceed at about equal rates, it was shown that some factor besides the heat of activation must govern the reactions, and it was suggested that this factor might be connected with a molecular phase—only those molecules reacting which possess the energy of activation and in addition are in a certain phase.

With regard to comparative measurements of the same reaction on different catalysts, glass, platinum, and silver were compared in respect of reaction (1) (Tingey and Hinshelwood, *ibid.*, 1922, **121**, 1668). Experiments have now been made with rhodium, gold, and palladium, which catalyse reaction (1), and with titanium dioxide, which catalyses reaction (2) almost exclusively.

The interest of the results with titanium dioxide lies in the comparison of the value of E_a for this catalyst with that for glass, which has the value 12,000–16,000 calories, a much lower value than is ever found for E_a . It seemed interesting to inquire whether a similarly low value for the apparent energy of activation would also be found for other catalysts, whether, that is, the small amount of energy required to activate the formic acid molecule for decomposition into carbon monoxide and water is essentially characteristic of this mode of reaction of the molecule. Since the value found is 29,500 calories, it appears that a small energy of activation for this mode of decomposition is not an inherent property of the formic acid molecule itself, which persists independently of the surface on which it is adsorbed.

There seems to have been no systematic survey of values for the energy of activation and of velocity constants for a specified reaction on a number of different catalytic surfaces. From the

results of this and previous investigations (*loc. cit.*) the following table has been made.

Surface.	E_{CO_2} .	Relative activity of the surface in promoting the reaction $\text{H}\cdot\text{CO}\cdot\text{OH} \rightleftharpoons \text{H}_2 + \text{CO}_2$ at 200°.
Duroglass	24,500	0.05
Gold	23,500	2
Silver	31,000	2
Platinum	22,000	100
Rhodium	25,000	500
Palladium		
(a) Freshly treated with an oxidising agent	39,000	25,000
(b) Containing occluded hydrogen	33,000	250

In this table, the values of E_{CO_2} are calculated, to the nearest 500 calories, by the equation $\log_e k_2/k_1 = \frac{E}{R} \left(\frac{T_2 - T_1}{T_2 T_1} \right)$. The numbers representing the relative rates of reaction refer to platinum as 100, and are calculated per unit superficial area of the catalyst. They are given only in round numbers, since the activity of a catalyst is very variable, and the superficial area is an approximate measure only of the effective surface.

The interpretation to be placed on the results naturally depends on the theory adopted as to the nature of the adsorbed layer. Only on the theory that the observed velocity is actually the rate of a slow chemical change of the adsorbed molecules has E any direct connexion with the stability of the molecule. In the present discussion, this is assumed, and Langmuir's theory that the adsorbed layer does not exceed one molecule in depth is adopted. The true value of E can only be obtained from the apparent value if the heat of adsorption is known. The heat of adsorption of such gases as ammonia by charcoal is usually about 4000 calories per gram-molecule, but there is reason to suppose that adsorption by porous materials like charcoal is a phenomenon of a different kind from the adsorption of gases by metals, and involves actual condensation of the gas in the capillary pores. From the results of Taylor and Burns (*J. Amer. Chem. Soc.*, 1921, **43**, 1273) on the adsorption of various gases by metallic catalysts the amounts adsorbed seem in many cases to be little influenced by a change of temperature from 25° to 110°. From this it may be concluded that the heats of adsorption are very small. We hope to attempt direct measurements of the adsorption of formic acid vapour, but in the meantime it is probably justifiable to conclude from analogy with the results of Taylor and Burns that the heat of adsorption is small and therefore that the values of E_{CO_2} , calculated from the

influence of temperature on the decomposition velocity, are very nearly equal to the true values.

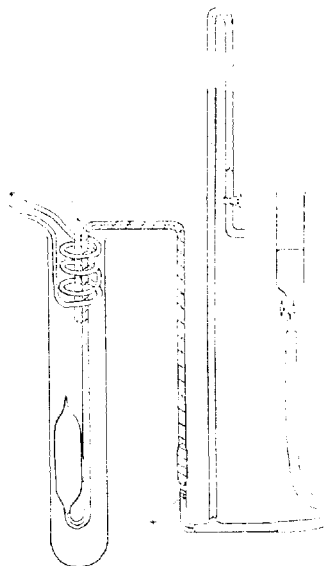
In the above table a lack of correlation between the values of E_{CO_2} and the relative activity of the catalyst shows that the relative velocity of reaction is not simply proportional to the number of molecules which would be expected from the kinetic theory to possess the requisite energy of activation. For the explanation of this lack of correlation, two possibilities are worth exploring. Either it may be assumed that on unit area of different catalysts widely differing numbers of molecules are adsorbed and actually participating in the reaction, or the divergence may be referred to a quite specific phase factor, by which the analogous lack of correlation between the values of E_{CO_2} and E_{CO} on glass and the relative rates of the corresponding reactions was explained. In this second case, we can make no further progress at present; on the other hand, if all the observed relations are interpreted simply in terms of the varying numbers of molecules adsorbed per unit area, then the results can be used to show how this number varies from one catalyst to another. We find, for example, that at 200° the surface of rhodium would have to be about one thousand times as thickly covered as that of gold. This calculation is based, however, upon the assumption that the phase factor is the same for the same reaction on different surfaces. At the end of this paper a tentative calculation is made of the fraction of the surface of different catalysts actually covered by adsorbed molecules of formic acid. The calculation depends on the assumption that Dushman's empirical equation (*J. Amer. Chem. Soc.*, 1921, **43**, 397) connecting the heat of activation with the absolute magnitude of the velocity constant of a homogeneous unimolecular reaction may be applicable to a reaction in a system of adsorbed molecules, which on the Langmuir theory is in effect a homogeneous reaction in two dimensions instead of three. These assumptions lead to the result that the adsorbed molecules cover a small fraction only of the surface. This is consistent with the experimental fact that the reaction is of the first order and not of zero order as it would be if the unimolecular layer were nearly complete.

The experimental methods employed were similar to those described in T., 1922, **121**, 1668, the course of the reaction being followed both manometrically and by heating known weights of 90 per cent. formic acid with the catalyst for varying times in a sealed bulb. The manometric apparatus previously described was modified so that weighed amounts of formic acid could be introduced in capillary tubes into the reaction vessel, which was then sealed off and evacuated through the tap before the formic acid

was vaporised. During evacuation the mercury reservoir was lowered sufficiently to leave a clear passage through the capillary manometer into the reaction bulb. After evacuation, the reaction bulb was immersed in the vapour-bath, and as the formic acid vaporised the mercury reservoir was gradually raised. Finally, the tap on the manometer tube was opened to the atmosphere and a series of readings of pressure and time were recorded.

A considerable number of sealed-bulb experiments were made at different temperatures to obtain statistical averages from which

FIG. 1.



the temperature coefficient of the reaction velocity might be calculated.

To obtain the temperature coefficient from a manometric experiment, the reaction was allowed to proceed at one temperature until about one-third of the formic acid had decomposed, the reaction vessel then being transferred to a bath at a higher temperature where the reaction was followed to completion. If in any case the values of k , the velocity constant, exhibited a drift, the temperature coefficient was obtained by extrapolating the value of k forwards for the lower temperature and backwards for the higher temperature, to a time midway between the last reading at the lower

temperature and the first reading at the higher temperature.

Analysis of the products of reaction was made as before in a Haldane apparatus.

Since measurements of reaction velocity were made at temperatures as low as 140°, the question of the association of formic acid vapour had to be considered. The pressure exerted by a known weight of 89.1 per cent. formic acid was measured at various temperatures in the manometric apparatus used for the decomposition experiments. In the following table, p_{obs} represents the observed total pressure in mm. of mercury exerted by the vapour,

while $p_{\text{calc.}}$ is the pressure which should be exerted by the known weight of formic acid vapour and water vapour in the bulb of given volume on the assumption that there is no association and that the gas laws are obeyed.

Temperature.	$p_{\text{calc.}}$	$p_{\text{obs.}}$	Ratio $p_{\text{calc.}}/p_{\text{obs.}}$
193.2°	1279	1209	1.058
184.0	1251	1171	1.069
153.9	1170	1028	1.138
138.2	1128	951	1.186
129.0	1103	884	1.248
115.3	1065	783	1.360

No decomposition occurred during the measurements. The differences between $p_{\text{calc.}}$ and $p_{\text{obs.}}$ above 140° are not sufficient seriously to affect the velocity measurements, especially as "end-points" were always observed directly.

Experiments were in all cases made to prove that the proportions of the different products of decomposition were not influenced by secondary interaction.

Experiments with Rhodium.—The rhodium was used in the form of foil. It catalyses the decomposition predominantly into carbon dioxide and hydrogen, although varying amounts of carbon monoxide and water are also produced. In measuring the latter reaction, however, it is difficult to allow for the effect of the glass bulb, which at the temperatures employed gives some carbon monoxide but practically no carbon dioxide. The reaction follows the unimolecular law fairly closely, although the velocity constant tends to rise in the later stages.

t (minutes).	p (mm. of H ₂).	$k = 1/t \log_e \frac{P_{\infty}}{P_{\infty} - p}$
7.7	44	0.0106
13.8	55	0.0104
18	94	0.0102
28	139	0.0102
36.5	176	0.0103
52.5	238	0.0105
62.5	272	0.0106
98.5	372	0.0110
186	518	0.0138
∞	561	

The following are the results of manometric experiments on rhodium:

Temperature.	$k_{\text{exp.}}$	$E_{\text{act.}}$ (cal./mole).
154.7	0.00388	25,900
185.2	0.0298	
155.1	0.00466	
185.2	0.0417	26,600
154.9	0.00559	
186.2	0.0378	23,800
Average		25,400

A series of sealed-bulb experiments over the same range of temperature gave for the mean of fourteen experiments in each case,

$$\left. \begin{array}{ll} 155.8^{\circ} & 1.47 \times 10^{-4} \pm 0.57 \times 10^{-4} \\ 182.2^{\circ} & 8.06 \times 10^{-4} \pm 3.1 \times 10^{-4} \end{array} \right\} 25,000 \text{ cal.}$$

A similar series of ten and eight experiments, respectively, at 185.7° and 212.7° gave 24,200 cal.

A series of experiments was also made over the range 140 – 154.7° , which gave values of E 29,900, 28,900, 29,900 from manometric experiments and 31,400 from the sealed-bulb experiments, but since the temperature range is too small to allow accurate measurements, and the association of formic acid begins to be appreciable at 140° , these results are discarded. The most probable value of E_{CO} is taken as 25,000 calories.

For comparison of rhodium with other catalysts, the average value of k_{CO} , calculated per square centimetre of rhodium foil, and referred to a bulb of 20 c.c. capacity, may be taken as 0.0024 at 200° . The unit of time is the minute and natural logarithms are used.

Experiments with Gold.—Gold produces decomposition almost exclusively into carbon dioxide and hydrogen, but its activity, in the form of foil, is not great. For the purpose of manometric experiments, therefore, gold was prepared in a state of fine subdivision by precipitation with oxalic acid from gold chloride solution.

Temperature.	k_{CO} .	E_{CO} .
140.5°	0.00217	23,600
185.0	0.0351	
140.0	0.00055	
185.0	0.0092	23,500

In order to obtain values for the velocity constant which should be comparable with those found for other catalysts, some experiments were carried out with foil of known area. The value of k_{CO} per unit area of gold foil and referred to a bulb of 20 c.c. capacity may be taken as roughly 0.0000092 at 200° . Gold shows thus only about 1/250 part of the activity of rhodium.

Experiments with Palladium.—All catalysts exhibit considerable variations, but the behaviour of palladium is quite exceptionally erratic. Its activity is considerable, and it catalyses the decomposition into carbon dioxide and hydrogen. The palladium was used in the form of smooth foil. It was anticipated that considerable difficulty would be occasioned owing to the occlusion of the hydrogen produced in the reaction, but this was found to occur to a comparatively small degree. Thus a piece of palladium foil

the activity of which was much greater than that of platinum or rhodium gave products the analysis of which was as follows: CO_2 0.487 c.c.; H_2 0.451 c.c.; CO 0.036 c.c. The area of the foil was 17 sq. cm. and about 20 c.c. of gas were produced, so that little hydrogen could have been occluded. After this foil had been used many times an analysis of the products gave CO_2 0.733 c.c.; H_2 0.567 c.c.; CO 0.012 c.c.

With regard to the variations in activity, which amounted to a hundredfold, it was concluded finally that when the surface of the palladium had been carefully cleaned with an oxidising agent, namely, chromic acid and sulphuric acid, it displayed very great activity, many times greater than that of rhodium, but that exposure to hydrogen diminished the activity very seriously. Although the absorption of hydrogen was never great, it occurred to some degree, so that presumably the structure of the palladium in the immediate neighbourhood of the surface was spongy, and the activity is greater when this region is free than when it is filled with dissolved hydrogen. The relative activity of palladium, as abulated in the introduction to this paper, is thus not strictly comparable with that of the other metals.

It seemed of little use to attempt to obtain very consistent values of E for palladium, but an approximate value was obtained by the manometric method. In one experiment, a freshly cleaned strip of foil of 4 sq. cm. surface was used. In the first part of the experiment, at 139.8° , the values of k were fairly constant, but in the second part, at 180.0° , they fell continuously from 0.0335 to 0.0156. By extrapolating, a value of 0.0360 was found. The value of E_{CO} , thus obtained was 39,000 calories. A second experiment was made without removing the palladium from the reaction bulb; at 140° , the rate was about one hundred times smaller than in the first experiment. The temperature was raised to 185.3° and subsequently to 212.1° . Between 140° and 185.3° , the value of E found was 31,500 calories, and between 185.3° and 212.1° 34,000 calories. The mean was taken as 33,000 calories.

Experiments with Titanium Dioxide.—This causes decomposition into carbon monoxide and water almost exclusively. The oxide used was in the form of powder; 1 gram was used in the sealed-bulb experiments; more for the manometric experiments. Fifteen sealed-bulb experiments were made at 138.4° and fifteen at 180.1° .

Temperature.	Average value of k , ...	E_{CO}
138.4°	0.000062	29,000
180.1	0.00163	

A manometric experiment showed that the reaction follows the unimolecular law and gave the values:

154.7°	0.000696	}	29,600
184.9	0.00696		

Discussion of Results.

The magnitude of the variation of reaction velocity with temperature may be equally well explained by the theory that a true rate of chemical change of the adsorbed molecules is being measured, and by the theory that the observed rate is a rate of diffusion of the reacting substance through an adsorbed layer the thickness of which diminishes rapidly with temperature. A third possibility may be suggested, which meets the objection that in the second case the adsorbed layer, small to begin with, would rapidly disappear as the temperature increased if it had to diminish rapidly enough to account for the change in reaction velocity. The possibility is that only those molecules can reach the surface of the catalyst and react, the kinetic energy of translation of which is sufficient to enable them to penetrate a permanent adsorbed layer of unchanging thickness such as the unimolecular films of carbon monoxide which are retained tenaciously by platinum. In this case, E would be a true energy of activation, but would represent translational and not internal energy. The objection, however, to both the second and third possibilities is that the two alternative modes of decomposition of formic acid on glass appear to be quite independent reactions, each with its characteristic heat of activation, in spite of the fact that in each case, according to the diffusion theory, a similar formic acid molecule would make its way through an identical adsorption layer. It is true that the relative speed of the two rapid reactions at the surface of the catalyst could vary with temperature, even although the observed total speed were governed by a diffusion process, but in this case the values of E for the two separate reactions could not be independently constant. Thus E_{co} on glass retains its characteristic value, which is very different from E_{co_2} , irrespective of whether the completing reaction is proceeding rapidly enough to account for more than half the total decomposition or is proceeding at a relatively inappreciable rate. The diffusion theory allows k_{co} and k_{co_2} to vary differently with temperature, but E_{total} would remain approximately constant while E_{co} and E_{co_2} would vary largely.

Approximate Calculation of the Relation between the True and Apparent Heats of Activation.—Let σ be the fraction of the surface covered for a given pressure of the adsorbed gas in the gas phase. Rate of condensation on surface $= a\sqrt{V}(1 - \sigma)$, where a = constant.

Rate of evaporation $= x\sigma$, where x = rate of evaporation per unit area covered at temperature T .

We may write $x = be^{-\lambda/RT}$,

where b = constant and λ is the heat of adsorption.

Equating rate of condensation and rate of evaporation,

$$a\sqrt{T}(1 - \sigma) = b\sigma \cdot e^{-\lambda/RT}.$$

If σ is small compared with unity, as it must be when the reaction follows the unimolecular law, then

$$\sigma = C\sqrt{T}e^{\lambda/RT}, \text{ where } C = \text{constant.}$$

If k is the velocity constant per unit area of catalyst, and k_0 is the velocity constant per unit area covered,

$$k = k_0\sigma = k_0C\sqrt{T}e^{\lambda/RT}.$$

But $k_0 = Be^{-Q/RT}$,

where Q is the true heat of activation and B is a constant.

Therefore $k = \text{constant} \sqrt{T}e^{-(Q-\lambda)/RT}$

$$\frac{d \log k}{dT} = \frac{1}{2T} + \frac{Q - \lambda}{RT^2} = \frac{Q - \lambda + \frac{1}{2}RT}{RT^2}.$$

But $d \log k/dT = E/RT^2$.

Therefore $E = Q - \lambda + \frac{1}{2}RT$

or approximately $E = Q - \lambda$.

Estimate of the Fraction of Surface Covered.—By making the assumptions referred to in the introduction, we may calculate the fraction of the surface covered in different cases in the following manner.

From the results of Tingey and Hinshelwood on platinum the value of k_{CO} , per square centimetre of platinum at 200° is 0.00044, the value referring to a bulb of 20 c.c. capacity. Dushman's empirical equation for the velocity constant of a unimolecular reaction is $k = \nu e^{-Nhr/RT}$,

where N = Avogadro's number and $Nhr = E$.

E_{CO} for platinum is 22,000 calories, whence $k = 15,000$, approximately, the unit of time being the second, or 900,000, the unit of time being the minute. But the observed value $k_{\text{obs}} = 0.00044$. Thus

$$\frac{\text{Number of molecules adsorbed}}{\text{Number of molecules in reaction bulb}} = \frac{0.00044}{900,000} = 5 \times 10^{-10}, \text{ approx.}$$

But under the experimental conditions there were in a 20 c.c. bulb about 6×10^{20} molecules; hence the total number adsorbed on 1 square centimetre of platinum is 3×10^{11} approximately. If a molecule of formic acid be assumed to occupy a space 5×10^{-8} $\times 5 \times 2$

cm. in length and breadth, then we shall find for the fraction of the surface covered a value of the order 10^{-3} .

In this way, the following rough values were obtained :

Surface.	k_{obs} at 200° per unit area.	Fraction of surface covered at about 2 atmospheres pressure.
Glass	0.00000025	5×10^{-8}
Gold	0.0000002	10^{-4}
Silver	0.0000103	10^{-1}
Platinum	0.00044	10^{-3}
Rhodium	0.0024	10^{-1}
Palladium	0.0010	150

It has already been pointed out that palladium is quite abnormal. With regard to the others, all that one can say is that the assumptions do not lead to any inconsistency with the modern theory of catalysis.

If the specific phase factor which was introduced to account for the lack of correlation between the values of E and the relative velocities of the two alternative reactions on glass is introduced here also, then the calculation is no longer valid, since Dushman's equation cannot be applied. Its application is really inconsistent with the previous conclusions, but it seemed of interest to see to what results it would lead. In a private communication, Prof. W. C. McC. Lewis has indeed suggested that the phase factor previously introduced might be interpreted in terms of different modes of adsorption. It is difficult to say whether formic acid could be adsorbed in two different ways on glass, but if this were possible the fractions of surface covered by the two differently adsorbed types of molecule would have to be very different. The question must be left open for the present.

Summary.

(1) Experiments on the kinetics of the heterogeneous decomposition of formic acid have been extended to include surfaces of rhodium, gold, palladium, and titanium dioxide.

(2) The significance of the "heat of activation" is discussed for the case of a heterogeneous reaction.

(3) Evidence is derived from the study of the thermal decomposition of formic acid in favour of Langmuir's adsorption theory.

(4) The heat of activation of the formic acid molecule for the reaction $\text{H}\cdot\text{CO}\cdot\text{OH} \rightleftharpoons \text{CO} + \text{H}_2\text{O}$ on titanium dioxide is found to be much greater than that of the same reaction on glass, so that the low value found for glass surfaces cannot be regarded as an inherent property of the free molecule.

(5) The values of E_{co} for a number of catalytic surfaces are

tabulated, and a lack of correlation is shown to exist between the values of E_{co} and the corresponding velocity of the reaction $\text{H}\cdot\text{CO}\cdot\text{OH} = \text{CO}_2 + \text{H}_2$. Two possible interpretations are pointed out. Either it may be assumed that a molecule must not only possess the critical energy, but must be in a certain phase before it decomposes, or the whole lack of correlation between E and k may be referred to the very widely differing fractions of the various catalytic surfaces which are actually covered with adsorbed molecules. If the second factor is *alone* operative, the actual fraction of surface covered can be calculated by assuming that Dushman's empirical equation for the velocity of a unimolecular reaction can be applied to the molecules actually adsorbed. This leads to values for the fraction of surface covered which are between 10^{-1} and 10^{-6} , except in the case of palladium, which behaves abnormally. These results are consistent with the modern theory of adsorption catalysis, but the application of Dushman's equation is inconsistent with the idea of a specific molecular phase governing the velocity of reaction, so that the choice between the alternatives is left open.

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[Received, March 27th, 1923.]

CXVI.—On the Propagation of the Explosion-Wave. Part I. Hydrogen and Carbon Monoxide Mixtures.

By HAROLD BAILEY DIXON and NOEL STANLEY WALLS.

Few experiments appear to have been published on the passage of the explosion-wave through mixtures of combustible gases. Berthelot, observing the slow rate of the wave through carbon monoxide and oxygen, as compared with electrolytic gas, measured the velocity of the explosion-wave through two mixtures of hydrogen and carbon monoxide-Knall-gas:

TABLE I.
Berthelot's Experiments.

Gases (vols.).			Rates in metres per second.	
CO.	H ₂ .	O ₂ .	Found.	Cal.
100	0	50	1090	1940
50	50	50	2008	2236
40	60	50	2170	2321
0	100	50	2810	2831

His formula (derived from the mean molecular velocity of the products of combustion), which agrees with the rate found for the explosion-wave in electrolytic gas, does not apply, he says, to the carbon monoxide; but with mixtures of hydrogen and carbon monoxide the formula holds good—"the hydrogen communicates to the carbon monoxide a law of detonation analogous to its own."

Again Berthelot measured the *initial* rates of the flame in hydrogen and in carbon monoxide Knall-gas, and then in a mixture of the two—timing the flame from the spark until it broke a "bridge" 130 mm. away; he also made a similar series with hydrogen and with ethylene Knall-gas. As these experiments were made in a closed bomb, the rates were measured during a period of acceleration and not do represent constant velocities of flame:

TABLE II.

Berthelot's Experiments.

Gases.	Time of travel of flame from spark through 130 mm. in thousandths of a second.
$2\text{H}_2 + \text{O}_2$	1.04
$2\text{CO} + \text{O}_2$	12.86
$\text{H}_2 + \text{CO} + \text{O}_2$	3.88
$2\text{H}_2 + \text{O}_2$	1.04
$2\text{C}_2\text{H}_4 + 6\text{O}_2$	2.86
$2\text{H}_2 + 2\text{C}_2\text{H}_4 + 7\text{O}_2$	1.37
	0.95 mean.
	1.95 mean.

Berthelot seems to have expected that the rates of the flame in the mixtures would be the arithmetical *means* of the individual rates; as the rates in the mixtures were found to be greater than the means, he concludes that the gases burn *separately*—the *hydrogen burning first* in each case.

More recently, Prof. Bone (*Proc. Roy. Soc.*, 1921, [A], **100**, 67) has made determinations of the time taken from the moment of firing until the maximum pressure is reached when explosive mixtures of hydrogen and carbon monoxide with air are fired in a closed bomb under 50 atmospheres initial pressure. He has shown that the interval between the spark and the maximum pressure is much less in the pure hydrogen than in the pure carbon monoxide Knall-gas, and he compares the time-intervals when different quantities of hydrogen replace carbon monoxide with the times calculated on the assumption that each explosive mixture carries the flame in turn at its own rate over lengths proportional to the volume of each present.

The "times" so calculated are of course the sum of the times taken by each explosive constituent; just as in a relay race the total time is the sum of the times taken by each runner over the

distance he is set to run. Prof. Bone shows that the calculated figures in no way agree with the rates he finds in the mixed gases; he directs attention to the great effect on the rate of combination when small quantities of hydrogen replace carbon monoxide in the explosive mixture, and (like Berthelot) he attributes this to the dominating influence of the hydrogen "which catalyses the reaction."

It is to be noted that in Bone's as in Berthelot's experiment the rate is measured from the firing point during the period of acceleration, and that in electrolytic gas the acceleration is more rapid and the explosion-wave is set up after a shorter run than in the case of damp carbon monoxide Knall-gas.

On the other hand, Dr. R. V. Wheeler and his fellow-workers have found that for the slow initial uniform phase of combustion of gases the rates for mixtures are the means of the individual maximum rates: thus "if on a speed-percentage graph the maxima for any two gases taken singly are joined by a straight line, all the maxima for mixtures of these gases lie approximately on this line."

It was found, for instance, that the highest initial rate (Le Chatelier's normal propagation by conduction) for a mixture of methane and air in a glass tube 2.5 cm. in diameter was 67 cm. per sec. when 9.9 per cent. of methane was present, and that the highest initial rate for a mixture of pentane and air in the same tube was 83 cm. per sec. when 2.92 per cent. of pentane was present. Now on mixing 77 volumes of the pentane-air gas with 23 volumes of the methane-air gas, the rate of uniform combustion was found to be 79 cm. per sec., the calculated rate on the straight line being 79.3 cm. per sec.

It has to be observed that these maximum rates for the slow propagation of flames through paraffin-air gases tend to a constant value, and therefore the rate of flame-propagation for any mixture of them would naturally lie close to a straight line joining the maxima of any pair.

But when hydrogen-air gas was mixed with methane-air gas, in a similar experiment, the rate of the flame fell short of the calculated rate by 15 per cent. It would appear, then, that mixtures containing hydrogen may not conform so closely to the "speed law."

Dr. Wheeler is of opinion that his speed law applies, not only to the initial phases of explosion, but also to the period of acceleration, and—with certain limitations—to the explosion-wave itself.

Lastly, in all the formulæ which have been proposed for calculating the velocity of the explosion-wave from the heat and volume changes in the reacting gases it has been assumed that the flame

proceeds as an intense compression-wave, and that its rate depends *inter alia* on the mean density of the gases concerned. Thus Prof. Jouguet has shown that the result of adding an equal volume of nitrogen or of hydrogen to electrolytic gas is a retardation or an acceleration of the wave which can be calculated from the mean densities of the mixtures.

There would seem, therefore, to be three different conceptions of the mechanism by which a flame may be propagated in explosive mixtures of gases: (i) that each kind of molecule formed in the flame-front may carry it forward in turn with its own velocity *over equal distances*; (ii) that each kind of molecule formed in the flame front may carry it forward with its own velocity *during equal intervals of time*; and (iii) that the propagation is independent of the motions of the individual molecules, but depends on their *mean velocity* and therefore on the mean density of the gases.

It thus became of interest to determine with some accuracy the rate of the explosion-wave in mixtures of hydrogen and carbon monoxide Knall-gas under uniform conditions, especially in those cases where only small quantities of the carbon monoxide were replaced by hydrogen; for by continuing the curve drawn through the rates found with diminishing quantities of electrolytic gas one may arrive at the "theoretical rate" for pure carbon monoxide Knall-gas—which is the "effective" rate used by Dr. Wheeler in his calculations.

The explosions were carried out in a coiled lead pipe of 12.5 mm. internal diameter; the distance between the two silver "bridges" was 69.156 metres. The "firing-piece" was a straight copper tube 1.45 metres in length; it joined the lead pipe through a full-bore tap, and was fitted at one end with a tap and firing-wires and at the other (close to the full-bore tap) with a small by-pass tap. The firing piece could thus be filled, through the lead coil, with the same mixture as that to be fired in the coil, or independently with electrolytic gas through the by-pass.

In the preliminary experiment the pendulum of the chronograph, moving a key, broke simultaneously the currents holding down the two styles, which registered their marks on the moving plate as they were pulled upwards by their springs: the two styles were then connected with the two silver bridges, and the key was connected with the coil and firing wires. On releasing the pendulum a second time, the movement of the key caused a spark to pass, and the flame passing along the firing-piece developed, after a shorter or longer run, the explosion-wave which broke the first bridge and traversing the coil broke the second bridge in turn. The two styles were therefore released in turn and registered their marks on the

moving plate. The interval between the two marks registered by the first style, *A*, gave the time between the passage of the spark and the breaking of the first bridge—independently of any error of the electro-magnet if the resistances of the circuits were properly adjusted; and similarly the interval between the two marks registered by the second style, *B*, gave the time between the passage of the spark and the breaking of the second bridge. The difference between these two intervals gave the time taken by the explosion wave to travel the known distance between the two bridges.

After proving the efficiency of our train of drying tubes by failing to fire the carbon monoxide Knall-gas, either by a direct spark, or by the shock of the explosion-wave set up in electrolytic gas filling the firing-piece, we proceeded to try the effect of replacing a very small quantity of carbon monoxide by hydrogen. We were at once struck by the fact that when the firing-piece was filled with electrolytic gas, and the mixture in the coil was fired by the shock of the rapidly moving explosion-wave generated in electrolytic gas, the rate in the mixture was distinctly lower than when the firing-piece was filled with the same mixture as in the coil.

In the following table are given the distances, *aa'*, between the marks of the first style (from spark to first bridge) and the distances, *bb'*, between the marks of the second style (from spark to second bridge) and the rates measured from the differences between them, (I) when the firing-piece was filled with electrolytic gas, and (II) when filled with the mixture in the coil :

TABLE III.

Gases	CO.	O ₂ .	H ₂ .
Volume	99.25	50	0.75
Style marks mm.			
	<i>a a'</i> .	<i>b b'</i> .	Rate in sec.
I	3.3	107.0	1701
	7.0	112.0	1680
	7.2	112.0	1684
	4.3	107.5	1710
Ia	5.9	109.7	1700
	5.2	109.4	1694
	3.6	108.0	1690
II	24.4	123.9	1759
	25.9	126.8	1745

Our first surmise—that some constriction between the firing-piece and the first bridge had damped down the explosion-wave in the manner discovered by Dr. C. Campbell—was shown to be unfounded when the experiments were repeated with a junction-piece with a

N N*

larger bore. The measurements made with the new junction-piece, tabled above under Ia, gave the same mean rate as before when the firing-piece was filled with electrolytic gas.

A similar discrepancy in the rates was found when a larger quantity of hydrogen was introduced; the rate was slower when the ignition was caused by electrolytic gas than when the firing-piece was filled with the mixture in the coil :

TABLE IV.

Gases	CO.	O ₂	H ₂
Volume	98.5	50	1.5
	Style marks mm.		
	<i>a a'</i>	<i>b b'</i>	Rate m.sec.
I	5.2	107.2	1731
	3.5	105.1	1738
	3.9	105.3	1740
II	19.3	118.9	1769
	15.8	115.4	1770

It remained now to determine whether the slower rate found with "electrolytic" firing was due to a temporary damping down of the explosion-wave at the junction of the two gas mixtures or to a permanent alteration in the nature of the explosion. A tube 14 metres in length was therefore introduced between the firing-piece and the first bridge, so that if the retardation was due to a temporary damping down of the flame at the junction of the two gases the explosion-wave might have time to be re-established before the flame reached the first bridge. It was found that, with this longer run, concordant results were obtained whether the firing piece were filled with electrolytic gas or with the mixture in the coil, and the rates agreed with the *faster* determinations previously made. The *mean* rates found for the explosion-wave in the two mixtures were :

CO.	O ₂	H ₂	Rate.
99.25	50	0.75	1754
98.5	50	1.5	1758

Further to test the question of the damping down and recuperation of the explosion-wave in carbon monoxide Knall-gas, experiments were made with small quantities of aqueous vapour in place of hydrogen. In the first sets (I), the firing-piece, filled with electrolytic gas, came close to the first bridge; in the second sets (II), the extra tube was introduced between the firing-piece and the first bridge to allow time for the recuperation of the wave :

TABLE V.

	CO.	O ₂ .	H ₂ O.	Rate.
I	99.25	50	0.75	1633
II	"	"	"	1661
I	98.5	50	1.5	1673
II	"	"	"	1708

The temporary damping down of the explosion-wave by "electrolytic firing" is thus shown to exist whether the carbon monoxide is made explosive by small quantities of hydrogen or by small quantities of steam. If it be true that pure carbon monoxide and oxygen do not combine with explosion because the product—carbon dioxide—would be above the temperature at which it would be mainly dissociated (H. B. Dixon, T., 1896, 69, 774), the same hypothesis might explain the discontinuity of the wave where the highly heated steam molecules, formed in the "electrolytic" wave-front, came into collision with the carbon monoxide mixture with its small hydrogen—or steam—content. In this zone of rapid molecular motion the oxidation of the carbon monoxide might be too slow to maintain the explosion-wave, just as it is in the explosion of cyanogen with twice its volume of oxygen, where the heated carbon monoxide as it is formed in the wave-front is inert towards oxygen, but combines with it slowly *behind the wave-front*.

It would follow from this hypothesis that, as the carbon monoxide is gradually replaced by more hydrogen in the mixed gases, the discontinuity should grow less and disappear; and at the other end of the scale where the carbon monoxide Knall-gas is fired with a great excess of electrolytic gas, the carbon monoxide should act largely as an inert gas and retard the wave as such. Both these anticipations have been verified: when 7.5 per cent. of the combustible gas was hydrogen, no discontinuity was found in the explosion-wave however the mixture was fired; when 7.5 per cent. of the combustible gas was carbon monoxide, the latter had practically the same retarding effect as an equal volume of nitrogen.

In Fig. 1, a line is drawn through the rates found for the unbroken explosion-wave when small quantities of hydrogen are substituted for carbon monoxide. The line is slightly curved and, continued backwards, cuts the speed ordinate for pure carbon monoxide Knall-gas close to 1750. We have therefore taken this as the "theoretical rate." It is in substantial agreement with the rate derived from the old experiments made thirty years ago in this laboratory; it was then found that carbon monoxide Knall-gas had a maximum rate of explosion of 1738 metres per second when it contained about 5.5 per cent. of water vapour.

At the other end of the curve the mean velocity found for pure electrolytic gas at 40° was 2810 m/sec., which is in close agreement with the old determinations—namely, 2821 m/sec. at 10° and 2790 m/sec. at 100° .

In the following table the means of the rates measured for various mixtures are set out, when hydrogen is made to replace the carbon monoxide step by step in the gas mixture— $2\text{CO} + \text{O}_2$; the total of the combustible gas being always 100 and the oxygen 50. In italics are given the rates, *A*, calculated from the distances travelled by each ingredient in equal times, and the rates, *B*, calculated from the times taken by each ingredient to travel equal distances.

FIG. 1.

Rates of explosion-wave in mixture $2\text{CO} + \text{O}_2$ when small quantities of H_2 replace CO.

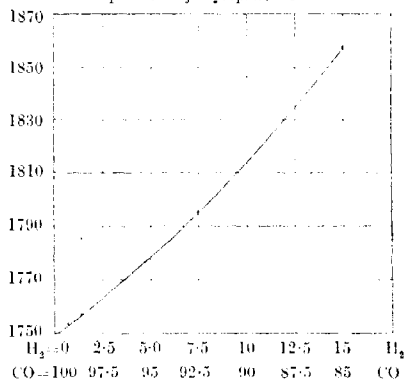


TABLE VI.

Rates of explosion-wave in mixtures of H_2 and CO-Knoll-gas compared with calculated rates.

CO.	100	98.25	98.5	92.5	85	62.5	50	25	15	7.5	0 CO.
H ₂ .	0	0.75	1.5	7.5	15	37.5	50	75	85	92.5	100 H ₂
<i>A.</i>											
Cal. rates											
1750		1758	1766	1830	1969	2117	2280	2515	2651	2730	2810
<i>Rates found (1750)</i>											
		1754	1758	1796	1858	2020	2130	2301	2507	2643	2810
<i>B.</i>											
Cal. rates											
1750		1755	1760	1799	1856	2038	2155	2439	2576	2688	2810

The measurements show that the velocities of the explosion-wave in the mixed gases follow the curve *B* closely at first, and do not deviate much from it so long as the hydrogen does not replace more than half the carbon monoxide; the rates found all appear to fall *below* the straight line, *A*, joining the two extremes.

As to the falling off in velocity when the hydrogen is in excess, we may recall the calculation of Jouguet, who gives the temperature in the wave-front of pure electrolytic gas as 3,956° Abs. At this temperature a small percentage of carbon dioxide added to the electrolytic gas would be largely dissociated; in other words, the carbon monoxide would be only partly burnt, and would act largely as an inert gas. In order to test this, experiments were made with mixtures containing 85 and 92.5 volumes of hydrogen with 15 and 7.5 volumes of nitrogen instead of carbon monoxide. In the first mixture the replacement of the 15 volumes of carbon monoxide by nitrogen was marked by a fall in rate of 24 metres per second, showing that the carbon monoxide was not wholly inert under these conditions: but in the second experiment, when 7.5 volumes of carbon monoxide were replaced by nitrogen, the rate fell only 3 metres per second.

TABLE VII.

<i>Rates of explosion-wave when CO is replaced by N₂.</i>						
CO Mixtures	H ₂	O ₂	CO	H ₂	O ₂	CO
Volume	85	50	15	92.5	50	7.5
Rates found	2507			2643		
N ₂ Mixtures	H ₂	O ₂	N ₂	H ₂	O ₂	N ₂
Volumes	85	50	15	92.5	50	7.5
Rates found	2483			2640		

Now the rates of these mixtures may be calculated approximately from the known rate of pure electrolytic gas on the assumption that, for small replacements, the rates will vary as the square roots of the absolute temperatures divided by the densities. Calculated in this way, the theoretical rate for the mixture 85H₂ + 50O₂ + 15N₂ would be 2480, and for the mixture 92.5H₂ + 50O₂ + 7.5N₂ would be 2638. The rates found by experiment for these two mixtures come exceedingly close to those calculated as above.

In these experiments some nitric oxide was formed by the union of the nitrogen with the excess of oxygen, as would be expected from the high temperature and the sudden cooling characteristic of the explosion-wave. Other experiments with oxygen only as the inert gas in place of the carbon monoxide gave rates somewhat slower than those found for the above mixtures; and experiments

with nitrogen only in place of the carbon monoxide Knall-gas gave rates slightly faster than those found for the above mixtures. These measurements leave no doubt that the carbon monoxide Knall-gas, when mixed with a large excess of electrolytic gas, is indistinguishable in its damping effect from a similar mixture of nitrogen and oxygen; the carbon monoxide appears therefore to be largely inert to the oxygen in the wave-front.

The Explosion of Mixtures of Hydrogen and Carbon Monoxide with Oxygen in Defect.

The experiments on the passage of the explosion-wave through mixtures of hydrogen and carbon monoxide with insufficient oxygen for complete combustion were made with the two objects—(i) of measuring the rates of the waves in the several mixtures, and (ii) of determining the division of the oxygen between the two combustibles under the conditions of the explosion-wave in a long tube. To insure that the division of the oxygen should not be affected by the removal of the steam from the sphere of action by condensation on the walls, it was found necessary to heat the tube to a temperature at which the pressure of saturated water-vapour would be greater than that exerted by the steam in the gaseous products of explosion at that temperature. The following experiments illustrate the difference between the end-products when the temperature of the tube is below or above the condensation-point of the steam formed in the explosion. After each explosion, the gases were blown out at one end of the tube by a current of air sent in at the other end, and samples of the products were collected over mercury. The volumes of carbon dioxide, carbon monoxide, and hydrogen were determined in a Bone and Wheeler apparatus; the volume of the carbon dioxide and carbon monoxide being equivalent to the carbon monoxide originally taken, and the volume of the hydrogen and water vapour being equivalent to the hydrogen originally taken:

TABLE VIII.

Effect of wall-temperature on the division of oxygen.

	Composition of mixture.			Temp.	Rate.	Composition of products.			Division of oxygen.	
	CO.	O ₂ .	H ₂ .			CO.	CO ₂ .	H ₂ .	H ₂ O.	$\frac{\text{CO} \times \text{H}_2\text{O}}{\text{CO}_2 \times \text{H}_2}$
I	75	25	25	45 ³	1945	46.0	29.0	5.0	20.0	6.3
				85	1947	43.8	31.2	6.2	18.8	4.3
II	50	25	50	40	2210	36.8	13.2	13.1	36.9	7.8
				85	2215	34.2	15.8	16.4	33.6	4.4
III	25	25	75	60	2608	4.2	20.8	28.8	46.2	7.9
				85	2614	5.6	19.4	32.7	42.3	4.5

In each of these experiments the volume was reduced by the combination of the oxygen from 125 to 100; therefore, when the gaseous products had assumed the temperature of the tube, the pressure was reduced from 760 mm. to 608 mm.

These experiments show that when the products of the incomplete combustion of hydrogen and carbon monoxide in the explosion-wave cool down under conditions where all four gases are free to react, the "water-gas equilibrium" is found to be nearly constant; but whenever there is a chance of the condensation of steam taking place during the secondary reactions the equilibrium is displaced. The metal tube is thus shown to have precisely the same effect on the secondary reactions after the explosion-wave as the glass endiometer was originally shown to have in the *ordinary* explosions of similar gas mixtures (*Phil. Trans.*, 1884, 175, 667).

In all our further experiments on the division of oxygen between the two gases the temperature of the tube was maintained between 85° and 90° in order to eliminate the chance of condensation.

The effect of small replacements of carbon monoxide by hydrogen in the mixture $4\text{CO} + \text{O}_2$ was next studied. When 1 or 2 per cent. of hydrogen only were present, the phenomena observed were closely analogous to those described in the complete combustion of similar mixtures: the explosion-wave was damped down temporarily when the mixture was fired by electrolytic gas. When an extra length of tube, filled with the mixture, was inserted between the firing tube and the first bridge, normal rates were obtained. When 5 per cent. or more of hydrogen were present the rates were normal, however the mixture was fired.

TABLE IX.

Mixtures.			Rates found.	
CO.	O ₂ .	H ₂ .	(i) Fired by ch. gas.	(ii) Fired by its own mixture.
99	2.5	1	1671	1747
98	2.5	2	1713	1755
95	2.5	5	1776	1776

When the rates obtained with the above mixtures are plotted against the percentage of hydrogen in the combustible gas, the points lie almost on a straight line, which, being continued backwards, cuts the speed-ordinate close to the rate 1740 m. per sec. This has therefore been taken as the theoretical rate for the explosion-wave in carbon monoxide when fired with one-quarter its volume of oxygen.

At the other end of the curve the mean value found for the explosion-wave in the mixture $4\text{H}_2 + \text{O}_2$ at 85° was 3284 metres

per sec. To test the question whether a small quantity of carbon monoxide replacing the hydrogen would be inert in the wave-front (as in the corresponding case where the combustible gas was wholly burnt), comparison-experiments were made with 15 and 7.5 per cent. of the hydrogen replaced by carbon monoxide and nitrogen, respectively. The following results were obtained :

TABLE X.

Mixture.	Rate.
$H_2 + O_2 + CO$	
85 25 15	2819
$H_2 + O_2 + N_2$	
85 25 15	2785
$H_2 + O_2 + CO$	
92.5 25 7.5	3015
$H_2 + O_2 + N_2$	
92.5 25 7.5	3000

When the hydrogen was replaced by carbon monoxide, the rates found were distinctly faster than those obtained with the same volume of nitrogen. It would seem, then, that the inertness of carbon monoxide, which appears to be a prominent factor when 7.5 per cent. of this gas replaces hydrogen in electrolytic gas, is no longer pronounced when the oxygen is reduced by one-half, and the temperature in the wave is correspondingly lowered.

In the following table are given the mean rates found for the explosion-wave when varying mixtures of carbon monoxide and hydrogen were *half-burnt* by oxygen: above the observed rates are given, *A*, the rates calculated from "equal times," and below are given, *B*, the rates calculated from "equal distances." The latter agree fairly closely with the observed rates for the mixtures containing small percentages of hydrogen; they diverge from the observed rates for mixtures containing more than 25 per cent. of hydrogen.

TABLE XI.

Rates of explosion-wave in mixtures of CO and H_2 when half the combustible gas is burnt.

H_2 , CO.	0	1	2	5	25	50	75	85	92.5	100	H_2 , CO.
		99	98	95	75	50	25	15	7.5	0	
<i>A</i> , Cal. [1749]		1755	1771	1817	2126	2512	2900	3052	3168	3284	
Rates found (1740)		1747	1755	1776	1952	2212	2614	2819	3015	3284	
<i>B</i> , Cal. [1749]		1748	1757	1782	1972	2275	2688	2898	3079	3284	

Rates of Explosion-Wave and Division of Oxygen in Electrolytic Gas Diluted with Carbon Monoxide.

In the following experiments the explosion-wave was transmitted through electrolytic gas diluted with successive additions of carbon monoxide in molecular proportions. The coil was maintained at 85°, and samples of the resulting gases were collected over mercury and analysed as before. The *mean* results are given below :

TABLE XII.

Mixture.	Rate m/sec.	$\frac{\text{CO} \times \text{H}_2\text{O}}{\text{CO}_2 \times \text{H}_2}$	= K.
$2\text{H}_2 + \text{O}_2 + \text{CO}$	2411	$\frac{19.4 \times 51.9}{13.9 \times 14.8}$	= 4.9
$2\text{H}_2 + \text{O}_2 + 2\text{CO}$	2215	$\frac{34.2 \times 33.6}{15.8 \times 16.4}$	= 4.4
$2\text{H}_2 + \text{O}_2 + 3\text{CO}$	2084	$\frac{44.5 \times 23.4}{15.5 \times 16.6}$	= 4.1
$2\text{H}_2 + \text{O}_2 + 5\text{CO}$	1876	$\frac{57.8 \times 14.3}{13.6 \times 14.3}$	= 4.2

Rates of Explosion-wave and Division of Oxygen in Carbon Monoxide Knall-gas Diluted with Hydrogen.

In a similar way the explosion-wave was transmitted through carbon monoxide Knall-gas diluted with successive proportions of hydrogen—the coil being maintained at 85°. The resulting gases were analysed as before. The *mean* results are given below.

TABLE XIII.

Mixture.	Rate m/sec.	$\frac{\text{CO} \times \text{H}_2\text{O}}{\text{CO}_2 \times \text{H}_2}$	= K.
$2\text{CO} + \text{O}_2 + \frac{1}{2}\text{H}_2$	1902	$\frac{20.4 \times 18.4}{59.6 \times 1.6}$	= 3.9
$2\text{CO} + \text{O}_2 + \text{H}_2$	2035	$\frac{29.5 \times 28.1}{37.2 \times 5.2}$	= 4.3
$2\text{CO} + \text{O}_2 + 2\text{H}_2$	2215	$\frac{34.2 \times 33.6}{15.8 \times 16.6}$	= 4.4
$2\text{CO} + \text{O}_2 + 4\text{H}_2$	2130	$\frac{28.9 \times 28.8}{4.4 \times 37.9}$	= 5.0

We have to thank the Scientific and Industrial Research Department for a grant which enabled one of us to devote his whole time to the research, and we are indebted to Mr. F. J. Hartwell, B.Sc., for assistance given in carrying out the experiments.

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[Received, February 27th, 1923.]

CXVII.—*Yohimbine (Quebrachine). Part II. apo-Yohimbine and Deoxy-yohimbine.*

By GEORGE BARGER and ELLEN FIELD.

IN a previous communication on the constitution of yohimbine (T., 1915, 107, 1025), we showed that by the action of cold concentrated sulphuric acid on the alkaloid a substance of the composition $C_{22}H_{26}O_6N_2S$ or $C_{21}H_{26}O_6N_2S$ * was produced. At the time we thought that sulphonation had taken place, and the name yohimbinesulphonic acid was accordingly suggested for the compound. A more detailed study of its properties, however, has shown us that this assumption is incorrect. Thus, although it dissolves readily in cold alkalis, and is reprecipitated unchanged on acidification, or in the case of solution in ammonia by prolonged boiling, when a solution in dilute sodium or potassium hydroxide is heated above 60° , sulphuric acid is eliminated with the production of a base $C_{22}H_{26}O_2N_2$, or $C_{21}H_{24}O_2N_2$, containing the elements of water less than yohimbine. The name *apoyohimbine* is suggested for it.† This ready removal of sulphuric acid is evidently inconsistent with the view originally expressed that the sulphy-group is attached to a benzene ring, but can be easily explained on the assumption that an alcoholic hydroxyl group present in yohimbine is esterified; evidence of the probable presence of a hydroxy-group has already been given by Spiegel (*Chem. Ztg.*, 1899, 23, 60), who has shown that the alkaloid yields an acetyl derivative on prolonged boiling with acetyl chloride. This hydroxyl evidently forms an ester with sulphuric acid, which, like ethyl hydrogen sulphate, can lose a molecule of the acid with the production of an ethylene linking. That the formation of *apoyohimbine* is accompanied by the introduction of such a linking into the molecule is proved by its catalytic hydrogenation to *dihydroapoyohimbine* (= *deoxy-yohimbine*), $C_{22}H_{28}O_2N_2$ or $C_{21}H_{26}O_2N_2$. The compound previously named yohimbinesulphonic acid is thus a sulphuric ester, and it is accordingly proposed to refer to it henceforth as yohimbine sulphuric ester.

Owing to the ease with which the methyl attached to the carboxyl in yohimbine sulphuric ester is removed by hydrolysis, the conversion of this compound into *apoyohimbine* does not take place quanti-

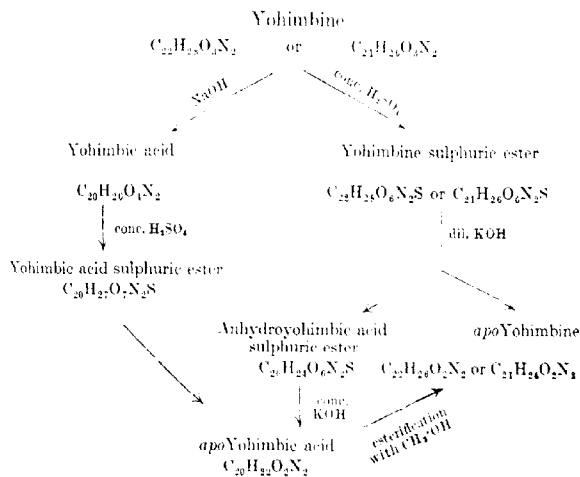
* In the course of this work no evidence has been obtained which permits of a choice between the formulae for yohimbine of Spiegel (*Ber.*, 1915, 48, 2084) with 22 carbon atoms and of Fourneau and Page (*Bull. Sci. Pharmacol.*, 1914, 21, 7) with 21 carbon atoms. We are now, however, convinced that yohimbic acid has 20 carbon atoms.

† Anhydroyohimbine would lead to confusion, since Spiegel has used this name for yohimbine itself, and subsequently abandoned it.

tatively. The two reactions, namely, (1) the removal of sulphuric acid with the formation of *apoyohimbine*, (2) the hydrolysis of the methyl ester grouping, proceed concurrently. It is proposed to name the product of the second reaction *anhydroyohimbic acid sulphuric ester*, $C_{20}H_{24}O_6N_2S$, for the reason that it contains the elements of water less than the corresponding compound, *yohimbic acid sulphuric ester*, $C_{20}H_{26}O_7N_2S$, which we have now prepared by the action of sulphuric acid on yohimbic acid itself. It will be recalled that yohimbic acid has the formula $C_{20}H_{26}O_4N_2$, and thus contains the elements of water more than would be expected if it were produced by the simple hydrolytic removal of the methyl ester grouping of yohimbine: evidently these elements are retained even after the treatment with concentrated sulphuric acid which is necessary for the conversion of yohimbic acid into the sulphuric ester.

It is remarkable that the sulphuric ester grouping in anhydroyohimbic acid sulphuric ester is much more stable than that in yohimbine sulphuric ester. Prolonged boiling with concentrated alcoholic potash, however, removes sulphuric acid, with the formation of *apoyohimbic acid*, $C_{20}H_{22}O_2N_2$, which on esterification with methyl alcohol yields *apoyohimbine*. Yohimbic acid sulphuric acid under similar conditions gives rise to the same acid, thus losing a molecule each of sulphuric acid and water.

The relationship between the various compounds described above is shown in the following scheme:



Dihydroapoyohimbine (= deoxy-yohimbine), prepared by catalytic reduction, has the hydroxyl group of the original alkaloid replaced by hydrogen; the two remaining oxygen atoms are in the carboxyl group. By elimination of this it should be possible to obtain an oxygen-free base. The hydroxyl of yohimbine is evidently present in a reduced ring, not in a benzene ring.

EXPERIMENTAL.

Hydrolysis of Yohimbine Sulphuric Ester. Formation of apo-Yohimbine and Anhydroyohimbic Acid Sulphuric Ester.—Five grams of yohimbine sulphuric ester were dissolved in the cold in 100 c.c. of a 2 per cent. solution of potassium hydroxide. The solution was then heated at between 60° and 80° and maintained at this temperature for a few minutes. apoYohimbine separated and was removed after cooling by repeated extraction with ether, in which it is somewhat sparingly soluble. The solution was then reheated to 80°, when a further separation of apoyohimbine took place which was again removed by ether. This process was repeated until no further precipitation occurred on boiling the solution for five minutes. The ethereal extract on evaporation yielded 1.5 grams of crystalline apoyohimbine. In repeated experiments where this procedure was adopted, the yield was found to be almost constant, amounting to 30 per cent. of the ester taken. When higher concentrations of alkali were used or when boiling was continued without removing the apoyohimbine at intervals as described above, the yield was diminished.

apoYohimbine crystallises in short, stout prisms melting at 251–252°. It is sparingly soluble in methyl or ethyl alcohol, benzene, chloroform, acetic acid, or ligroin, and moderately soluble in ether. The free base is somewhat unstable, becoming coloured on exposure to light, or on prolonged heating at 120°. A solution in glacial acetic acid acquires a yellowish-green fluorescence on standing. It is optically active, having $[\alpha]_D$ about + 40°, but owing to the colour of the solution, the rotation could not be observed with very great accuracy.

The hydrochloride is produced by the addition of hydrochloric acid to an alcoholic solution of the base, or of ammonium chloride to a solution in dilute acetic acid. It is characterised by its very slight solubility in water (1:1300 at room temperature) and the beautiful, glistening, rhomb-shaped plates which it forms on recrystallisation from hot aqueous alcohol. It melts at 299–300° with decomposition (Found: C = 67.93; H = 6.79. $C_{22}H_{26}O_2N_2$. HCl requires C = 68.30; H = 6.98. $C_{21}H_{24}O_2N_2 \cdot HCl$ requires C = 67.65; H = 6.71 per cent.).

After removal of apoyohimbine, the mother-liquor yielded on acidification with hydrochloric acid 2.5 grams of an amorphous precipitate of anhydroyohimbic acid sulphuric ester. It was purified by dissolving in ammonia and acidifying the hot dilute solution with hydrochloric acid. Radiating prisms separated as the solution cooled.

Anhydroyohimbic acid sulphuric ester is readily soluble in alkalis, acetic acid, or aqueous alcohol, but very sparingly soluble in water (Found: C = 57.20; H = 5.85. $C_{20}H_{24}O_6N_2S$ requires C = 57.14; H = 5.71 per cent.).

Hydrolysis of Anhydroyohimbic Acid Sulphuric Ester. Formation of apoYohimbic Acid.—Five grams of anhydroyohimbic acid sulphuric ester were heated for two hours with 15 c.c. of 40 per cent. potassium hydroxide in 75 per cent. alcohol. After evaporation of the alcohol, the potassium salt of apoyohimbic acid solidified. It was dissolved in hot water and the solution acidified strongly with hydrochloric acid. A micro-crystalline precipitate of the hydrochloride of the acid separated. It was purified by solution in ammonia and reprecipitation with hydrochloric acid.

apoYohimbic acid hydrochloride crystallises in rosettes of prisms melting at 301° with decomposition (Found: C = 66.87; H = 6.38. $C_{20}H_{22}O_2N_2.HCl$ requires C = 66.94; H = 6.41 per cent.). It is moderately soluble in hot water, but, owing to hydrolysis of the salt, separates as a gel on cooling, and can only be crystallised in the presence of a considerable excess of hydrochloric acid.

The free acid could not be obtained in a crystalline condition, probably owing to its amphoteric nature. Neutralisation of the potassium salt with acetic acid produced only an amorphous precipitate which was doubtless a mixture of acid and acetate.

Esterification of apoYohimbic Acid.—One gram of apoyohimbic acid hydrochloride, suspended in 50 c.c. of methyl alcohol, was saturated with dry gaseous hydrogen chloride. During this process solution gradually took place, and after standing for two hours the ester hydrochloride separated. It was identified as apoyohimbine hydrochloride by the characteristic form of the crystals, its sparing solubility, and its melting point. Further, the free base had a melting point of 252° which was not lowered when it was admixed with apoyohimbine.

Yohimbic Acid Sulphuric Ester and its Hydrolysis.—In the preparation of yohimbic acid sulphuric ester in quantity it was found very difficult to prevent the yohimbic acid from forming a sticky cake into which the sulphuric acid could not penetrate, and this difficulty was overcome by grinding the yohimbic acid with fine sand.

Ten grams of yohimbic acid were ground in a mortar with twice its bulk of sand, 30 c.c. of concentrated sulphuric acid were then added, and the grinding was continued until the yohimbic acid had dissolved to form a thick, syrupy liquid above the sand. The mixture was then poured on ice and the precipitated ester collected by the aid of the pump. An almost complete mechanical separation from the sand can be effected by stirring and decantation of the lighter precipitate from the heavy sand. The last traces of yohimbic acid sulphuric ester were finally removed from the sand by solution in ammonia and reprecipitation by dilute hydrochloric acid after filtration. Yield 9 grams. (In the preparation of large quantities of yohimbine sulphuric ester, the same procedure was adopted.)

Yohimbic acid sulphuric ester is best purified by solution in ammonia and acidification of the hot solution with dilute hydrochloric acid. It crystallises in fan-shaped clusters of needles, and is very sparingly soluble in water and most other neutral solvents, and readily soluble in alkalis (Found: C = 54.77; H = 5.98. $C_{20}H_{26}O_7N_2S$ requires C = 54.79; H = 5.93 per cent.).

The hydrolysis was carried out under similar conditions to those described above for anhydroyohimbic acid sulphuric ester. The acid derived from the hydrolysis was purified as the hydrochloride, which melted at 301° , and gave the following results on analysis, proving it to be identical with *apoyohimbic acid* (Found: C = 66.49; H = 6.35. $C_{20}H_{24}O_2N_2 \cdot HCl$ requires C = 66.94; H = 6.41 per cent.).

Deoxy-yohimbine. Five grams of *apoyohimbine* were dissolved in 100 c.c. of 10 per cent. acetic acid, and reduced by means of hydrogen under an excess pressure of one and a half atmospheres, using palladium chloride and a little gum arabic as catalyst, according to the method described by Skita (*Ber.*, 1911, **44**, 2863). Slightly more than the theoretical volume of hydrogen for addition of two hydrogen atoms was absorbed during the space of about four hours. The solution was then made alkaline with ammonia and the precipitated base shaken out with ether. After removal of the ether, the product was recrystallised from methyl alcohol, and melted at $200-203^\circ$. *Deoxy-yohimbine* crystallises in long-slender prisms which are sparingly soluble in ether, alcohol, or ethyl acetate, and is considerably more stable than *apoyohimbine*, showing no tendency to darken on exposure to light or on heating at 160° (Found: C = 74.02; H = 7.56. $C_{22}H_{28}O_2N_2$ requires C = 75.00; H = 7.93. $C_{21}H_{26}O_2N_2$ requires C = 74.55; H = 7.69 per cent.). Like *apoyohimbine*, it gives a sparingly soluble hydrochloride.

The yohimbine employed in this research was partly purchased with a grant from the Moray Research Fund of this University, and partly presented to us by Messrs. Hoffmann-Laroche, of Basle. For both kinds of assistance we wish to record our thanks.

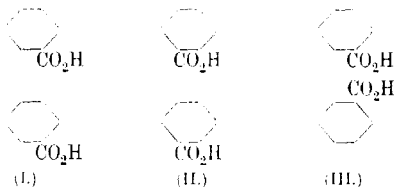
DEPARTMENT OF MEDICAL CHEMISTRY,
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[Received, March 29th, 1923.]

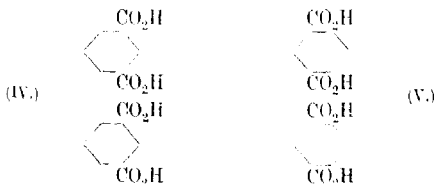
CXVIII.—*The Molecular Configurations of Polynuclear Aromatic Compounds. Part III. Diphenyl-3:5:3':5'-tetracarboxylic Acid.*

By HAROLD BURTON and JAMES KENNER.

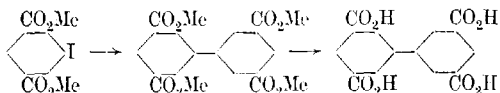
IN the course of a discussion some years ago of Kauffler's formula for diphenyl (Kenner, T., 1913, **103**, 618), attention was directed to the observation of Ullmann (*Annalen*, 1904, **332**, 73) that diphenyl-3:3'-dicarboxylic acid does not furnish an anhydride, and thus differs from ordinary diphenic acid. It was pointed out that this difference would be evidence against an equivalence of the 3:3'- and the 2:2'-positions in diphenyl, such as would be involved in the formulæ (I) and (II) in which the planes of the two benzene nuclei are parallel, unless Ullmann's compound were in reality a 3:5'-derivative (III). This reservation acquired greater significance



when a second form of 6:6'-dinitrodiphenic acid was discovered (Kenner and Stubbings, T., 1921, **119**, 593), and became even more pertinent when it was shown that the synthetic form of this acid, prepared in the same manner as the above 3:3'-dicarboxylic acid,



was probably to be looked on as a *trans*-acid, with carboxyl groups occupying the 2- and 6'-positions, if its formula were of the Kauffer type (Christie and Kenner, T., 1922, **121**, 614). Obviously the deficiency thus indicated in the above argument might be repaired by an investigation of *diphenyl-3 : 5 : 3' : 5'-tetracarboxylic acid* (IV). This acid was therefore synthesised by the usual process, which is represented by the following scheme :



The acid was not converted into an anhydride by boiling with acetic anhydride, but was recovered unchanged.

This result was obtained two years ago, and is now published in view of the appearance of a paper dealing with the configuration of benzidine (Adams, Bullock, and Wilson, *J. Amer. Chem. Soc.*, 1923, **45**, 521), in which reference is made to the non-formation of an anhydride from diphenyl-3 : 3'-dicarboxylic acid as evidence against Kauffer's formula in the case of this compound, but without mention of the possibility above explained. Publication had been previously withheld, because further work became desirable when other experiments performed in this laboratory by Mr. W. V. Stubbings showed that failure to obtain an anhydride from the above tetracarboxylic acid is not such decisive evidence against the Kauffer formula as it would at first sight appear to be. It could only be so if diphenyl-2 : 6 : 2' : 6'-tetracarboxylic acid (V) should furnish an anhydride in the same manner as diphenic acid does. The results of Mr. Stubbings's work, however, were in agreement with the observations of Mayer (*Ber.*, 1913, **46**, 2298), who was unable to prepare an anhydride from this tetracarboxylic acid. A further point of difference between this acid and diphenic acid is seen in the fact that the chloride of the tetracarboxylic acid is easily obtained by the usual means, whereas attempts to prepare that of diphenic acid usually result in formation of the anhydride. This observation is not an isolated one, for Schmidt was similarly unable to prepare the anhydride of 4 : 4'-dinitrodiphenic acid (*Ber.*, 1903, **36**, 3743). It is hoped to return to this point in the near future, and it is clear that the diphenyltetracarboxylic acids require further examination.

EXPERIMENTAL

m-Iodoisophthalic acid was prepared according to the directions of Grahl (*Ber.*, 1895, **28**, 85). Its *methyl* ester forms small needles,

m. p. 104–105°, whilst the *ethyl* ester consists of small prisms, m. p. 76° (Found: C = 40.93; H = 3.45. $C_{12}H_{13}O_4I$ requires C = 41.38; H = 3.73 per cent.).

Diphenyl-3 : 5 : 3' : 5'-tetracarboxylic Acid.—The methyl and ethyl esters were prepared by gradual addition of copper powder to an equal weight of the corresponding esters of *m*-iodoisophthalic acid at 220°, and finally heating the whole at 250°. This is necessary because the meta-orientation of the carbalkyloxy-groups with respect to the iodine atom appreciably diminishes the reactivity of the latter. After extraction with benzene, and further crystallisation from this solvent, the *methyl* ester was obtained in prisms, m. p. 209°, whilst the *ethyl* ester formed minute prisms, m. p. 146–147° (Found: C = 65.36; H = 5.95. $C_{24}H_{26}O_8$ requires C = 65.16; H = 5.88 per cent.).

The *acid*, prepared from the esters by alkaline hydrolysis, was insoluble in the ordinary solvents, but separated after dilution of its solution in concentrated sulphuric acid in microscopic prisms, which melted above 300° (Found: C = 57.72; H = 3.45; equivalent = 81.5. $C_{12}H_6(CO_2H)_4$ requires C = 58.18; H = 3.03 per cent.; equivalent = 82.5].

The *chloride* crystallised from benzene in small prisms, m. p. 128°. The *amide*, prepared from the chloride, formed very small needles, melting above 300°, and sparingly soluble in the usual solvents (Found: N = 17.08. $C_{16}H_{14}O_4N_4$ requires N = 17.17 per cent.). The sparingly soluble *anilide* formed small prisms, which blackened without melting at 280° (Found: N = 8.84. $C_{20}H_{18}O_4N_4$ requires N = 8.88 per cent.).

When the acid (2.5 grams, equivalent = 81.5) was boiled for ten hours with acetic anhydride (50 c.c.), it was recovered (equivalent = 81.6) after allowing the mixture to cool, collecting the solid material, thoroughly washing it with dry benzene, and drying it at 120°.

One of us (H. B.) expresses grateful acknowledgment of a grant from the Scientific and Industrial Research Committee which enabled him to participate in this work.

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Received, March 14th, 1923.]

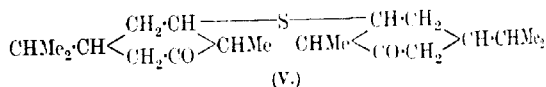
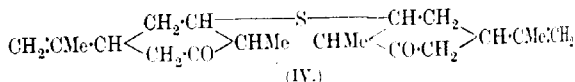
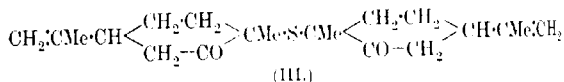
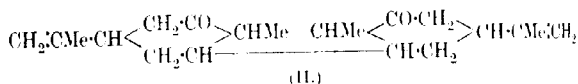
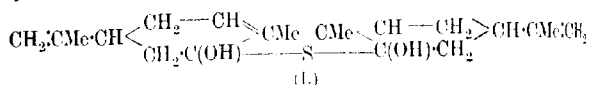
CCIX.—*The Interaction of Hydrogen Sulphide, Thiocyanogen, and Thiocyanic Acid with Unsaturated Compounds.*

By FREDERICK CHALLENGER, ALAN LAWRENCE SMITH, and
FREDERIC JAMES PATON.

THE additive products obtained from two molecules of carvone or carvotanacetone and one of hydrogen sulphide in alcoholic ammoniacal solution have been investigated by a number of chemists without the exact constitutions having been determined.

From the fact that carvone hydrosulphide does not react with phenylhydrazine* or semicarbazide, Harries and Stirn (*Ber.*, 1901, **34**, 1931) suggested the constitution (I). Wallach ("Terpene und Campher," 1909, p. 63), owing to the behaviour of many $\alpha\beta$ -unsaturated ketones on reduction, including carvone which gives dicarvelone (II), prefers the constitution (III).

This type of structure is supported by the work of Steele (P., 1911, **27**, 240), who showed that the hydrosulphide reacts with hydrogen cyanide, giving an unsaturated dinitrile containing four double bonds, two of which arise by elimination of water from the dicyanohydrin. He suggested the formula (IV).



As the formula of Harries and Stirn contains four double bonds, and the Wallach-Steele structures only two, it appeared probable that

Carvone also is stated to be inert towards phenylhydrazine (Ohta and Piatti, *Gazzetta*, 1922, **52**, ii, 333).

titration of the hydrosulphide with bromine in chloroform solution at -15° would afford decisive evidence.

The results we obtained clearly indicated the presence of two double linkings only. This was confirmed by the isolation and analysis of *carvone hydrosulphide tetrabromide*, which melts and decomposes at $110-115^{\circ}$.*

When *dl*-carvotanacetone hydrosulphide† (m. p. $205-207^{\circ}$) was treated with bromine at -15° , no decoloration took place. This behaviour is strong evidence that constitutions IV and V should be assigned to the two hydrosulphides.

After our work was concluded, we found that according to Ziem (*Diess.*, Leipzig, 1912, p. 19) carvone hydrosulphide reacts with four atoms of bromine; a crystalline bromide was, however, not isolated. Experimental details are not given, and the work does not appear in the main communication of Deussen and Ziem (*J. pr. Chem.*, 1914, [ii], 90, 318).

Formula (III) is also in agreement with our results, but in view of the general behaviour of $\alpha\beta$ -unsaturated ketones towards ammonia, hydroxylamine, and sodium hydrogen sulphite, the negative sulphur atom must be regarded as attached to the β -carbon atom.

Attempts to prepare an oxime or a methyl iodide additive product from the two hydrosulphides were unsuccessful, hydrogen sulphide being liberated. With zinc and acetic or hydrochloric acid, hydrogen sulphide was eliminated from carvone hydrosulphide even in the cold, and with zinc dust and ammonium chloride on heating. Hydrogen in presence of colloidal palladium failed to react with an ethyl acetate solution.

*iso*Thujone, prepared according to Wallach's method (*Annalen*, 1895, 286, 102; 1915, 408, 164), and therefore containing traces of carvotanacetone, gave a very small amount of solid product, but the bulk of the ketone did not react with alcoholic ammonium sulphide. Carvenone behaved similarly. Phenyl β -methylstyryl ketone, $\text{CMePh}\cdot\text{CH}\cdot\text{COPh}$, readily reacted, probably giving a mixture of compounds analogous to those obtained by Fromm (*Annalen*, 1912, 394, 290). Dihydrocarvone, tetrahydrocarvone,

* The possibility that this compound is in reality a partial substitution product, for example, dibromocarvone hydrosulphide dihydrobromide, would appear to be excluded by the stability towards bromine of carvotanacetone hydrosulphide, where substitution might equally be expected.

† *dl*-Carvotanacetone was prepared by boiling thujone for several days under reflux, fractionating, and collecting between 222 and 232° . Much formation of resinous matter was observed. If, instead of isolating pure thujone, tansy oil was similarly treated, the conversion to carvotanacetone took place more slowly (compare Semmler, *Ber.*, 1894, 27, 895).

pulegone, thujaketone, methylheptenone, pinene, limonene, amylene, terpineol, isosafrole, anethole, and cinnamic acid did not react.

It may be mentioned that in the absence of ammonia or other base carvone hydrosulphide does not appear to be formed.* Fromm (*loc. cit.*) on the other hand, describes compounds formed by simultaneous addition of both ammonia and hydrogen sulphide to benzylideneacetone. Experiments are now in progress with a view to determine (a) why so many $\alpha\beta$ -unsaturated ketones do not combine with hydrogen sulphide, (b) the part played by the ammonia in the reaction. In connexion with another research, our attention was directed to the properties of thiocyanogen, and it appeared possible that, by studying the reactions of this radicle with unsaturated compounds, results might be obtained which would not be without some bearing on the behaviour of hydrogen sulphide.

The reactions of thiocyanogen described by Söderbäck (*Annalen*, 1919, 449, 217) may be divided into two main classes. In one type of reaction, the radicle combines directly with metals such as iron, mercury, and cadmium, to form the respective thiocyanates, or with cuprous thiocyanate, giving rise to the cupric salt. The second type of reaction is a substitution, since with aniline, dimethylaniline, and phenol the corresponding *p*-thiocyano-derivatives and thiocyanic acid are formed. With mercury diphenyl, one aryl group is eliminated as phenyl thiocyanate and mercury phenyl thiocyanate produced. In these and most of its reactions, thiocyanogen exhibits a close relation to the halogens. The direct addition of thiocyanogen to organic compounds is not described by Söderbäck or seemingly by any later worker. Challenger and Wilkinson (T., 1922, 121, 101) have shown that triphenylbismuthine dithiocyanate, $\text{Ph}_3\text{Bi}(\text{SCN})_2$, cannot be isolated from the interaction of thiocyanogen and the bismuthine. An attempt to prepare this substance from triphenylbismuthine dichloride and lead thiocyanate also failed, the products in each case being diphenylthiocyanobismuthine and phenyl thiocyanate. Similar results were obtained with tri- α -naphthylbismuthine and its dichloride.

These reactions further illustrate the analogy between thiocyanogen and iodine which was first referred to by Söderbäck (*loc. cit.*). Since di-iodides of tertiary aromatic stibines (*Annalen*, 1886, 233, 51) and arsines (*ibid.*, 1902, 321, 203) are known, whilst tertiary bismuthine di-iodides do not exist, it appeared probable that stable additive products might be obtained from thiocyanogen and tertiary stibines, arsines, and possibly phosphines. Although such com-

* The hydrosulphide is formed, however, by passing hydrogen sulphide into an alcoholic solution of carvone containing solid anhydrous sodium carbonate.

pounds might be expected to have little tendency to lose aryl thiocyanate, owing to the relative stability of derivatives of quinquivalent antimony, arsenic, and phosphorus, their susceptibility towards hydrolysing agents appeared very probable. Triphenylarsine dichloride, for example, is readily converted by atmospheric moisture into the hydroxychloride (Michaelis, *Annalen*, 1902, 321, 162), whilst triphenylarsine cyanobromide, $(C_6H_5)_3As(CN)Br$, similarly yields triphenylarsine hydroxybromide (Steinkopf and Schwen, *Ber.*, 1921, 54, [B], 2791). Triphenylphosphine cyanobromide is even more sensitive to moisture, being converted into triphenylphosphine oxide, both negative groups being hydrolysed, unless special precautions are observed (Steinkopf and Buchheim, *ibid.*, p. 1024).

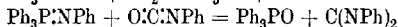
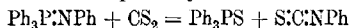
The results now to be described are in agreement with these expectations. With an ethereal solution of thiocyanogen, triphenylstibine yields *triphenylstibine dithiocyanate*, $(C_6H_5)_3Sb(SCN)_2$, m. p. $105-106^\circ$, but no phenyl thiocyanate. On boiling with water, this is converted into the *hydroxythiocyanate*, $(C_6H_5)_3Sb(OH)SCN$, m. p. 228° . A mixture of the dithiocyanate with a small amount of this hydroxy-derivative is obtained from triphenylstibine dichloride and lead thiocyanate in dry benzene. This reaction and the fact that the dithiocyanate on boiling with alcoholic silver nitrate is converted into triphenylstibine hydroxynitrate prove the thiocyanogroups to be attached to antimony and not to the benzene nucleus.

A compound, $(C_6H_5)_3Sb \cdot 2HSbSCN$, which would give very similar analytical results, might be expected to yield triphenylstibine under these conditions. Such an additive product could only be produced in the reactions just described if relatively large amounts of water were present, whereas dry solvents were used. This conclusion is further strengthened by the fact that triphenylstibine and triphenylarsine are both recovered unchanged from ethereal solutions of thiocyanic acid, prepared by Klason's method (*J. pr. Chem.*, 1887, [ii], 35, 407).

The behaviour of triphenylarsine towards an ethereal solution of thiocyanogen differs from that of triphenylstibine in that a dithiocyanate is not obtained. The product is *triphenylarsine hydroxythiocyanate*, m. p. 110° , which is also obtained when either triphenylarsine dichloride or hydroxychloride is shaken with dry lead thiocyanate in dry benzene. Its production is probably due to the action of traces of moisture on the unknown dithiocyanate. It is interesting to notice in this connexion that triphenylarsine dichloride is much more susceptible to moisture than the corresponding stibine derivative.

In the case of triphenylphosphine and thiocyanogen, it was

expected that triphenylphosphine oxide would be produced from the action of traces of moisture on the, presumably very reactive, triphenylphosphine dithiocyanate. With ethereal solutions of thiocyanogen or of thiocyanic acid, the product was, however, triphenylphosphine sulphide (*Annalen*, 1885, 229, 307). This reaction recalls the production of triphenylphosphine sulphide and oxide from triphenylphosphinephenylimine and carbon disulphide and phenylcarbimide, respectively :



(Staudinger and Hauser, *Helv. Chim. Acta*, 1921, 4, 866, 871). With triphenylbismuthine and thiocyanic acid, the reaction differs from that with thiocyanogen, since benzene, diphenylthiocyanobismuthine (Challenger and Wilkinson, *loc. cit.*), and probably phenyldithiocyanobismuthine are produced, but no phenyl thiocyanate.

Some difficulty was experienced during the estimation of nitrogen in the thiocyno-derivatives of triphenylstibine and triphenylarsine by the Dumas method, even when half the copper oxide was replaced by lead chromate. In the case of triphenylstibine dithiocyanate, if the combustion was carried out at the usual rate, very high and varying results were obtained, for example, 8.8 and 11.0 instead of 6.0 per cent. In one case, the gas (which had a sweet odour) was exploded with oxygen, when a diminution in volume of about 75 per cent. occurred. Since carbon oxysulphide, which might conceivably be produced during the combustion, would almost certainly have disappeared on long standing in contact with potassium hydroxide (Stock and Kuss, *Ber.*, 1917, 50, 160), the impurity was probably carbon monoxide, methane, or ethylene. Nitric oxide was absent. By very slow and cautious combustion at a high temperature normal results were obtained.

The behaviour of these thiocyanates resembles that of acetonitrile, which was found by Dunstan and Carr (*P.*, 1896, 12, 48) to give high results for nitrogen unless the combustion were carried out very slowly. This they attributed to the formation of methane, which was also responsible for the abnormal nitrogen figures observed by Haas (*T.*, 1906, 59, 570) with various bases obtained from dimethyldihydroresorcinol and aromatic primary amines and diamines. Similar results are described by Guareschi (*Atti R. Accad. Sci. Torino*, 1907, 42, 79) and by Davis (*P.*, 1906, 22, 81, discussion).

EXPERIMENTAL.

Action of Halogens on Carbon Hydrosulphide.—When chlorine (4 atoms), dissolved in chloroform, was added to a similar solution

of the hydrosulphide at 20°, hydrogen chloride was evolved. The product contained chlorine and sulphur, but did not crystallise, and was probably a mixture. With excess of chlorine and less careful cooling, hydrogen sulphide was eliminated. In chloroform at room temperature, bromine decomposed the hydrosulphide, hydrogen bromide, hydrogen sulphide, and sulphur bromide being formed. Iodine and its monochloride and monobromide gradually gave hydrogen sulphide in the cold. The same result was obtained with dry hydrogen chloride in glacial acetic acid.

Analysis of the Hydrosulphide.—A cold, dilute solution of bromine in chloroform was run slowly from a burette into a similar solution of carvone hydrosulphide at -15° , until a faint permanent red colour was produced. Excess of bromine was estimated with sodium thiosulphate solution (0.2497 gram of hydrosulphide absorbed 4.30, 4.25, 4.00 c.c. of bromine solution. Two double linkings require 4.65 c.c.). On addition of more bromine at -15° , the colour was only very slowly discharged, hydrogen bromide and sulphide being evolved.

Isolation of the Tetrabromide.—Carvone hydrosulphide (4.49 grams) in 150 c.c. of chloroform was treated with 4.3 grams of bromine in 160 c.c. of chloroform at -15° . An equal volume of light petroleum was then added, when a white solid was deposited. This was washed with light petroleum and purified by solution in cold chloroform and reprecipitation as before (Found: Br = 48.51, 48.70; S = 4.92, 4.92. $C_{20}H_{30}O_2Br_4S$ requires Br = 48.87; S = 4.88 per cent.). The tetrabromide melts and decomposes at 110–115°.

Action of Hydroxylamine on Carvone Hydrosulphide.—The hydrosulphide (12 grams), hydroxylamine hydrochloride (5 grams), and methyl alcohol (40 c.c.) were left for thirty-six hours at room temperature, when hydrogen sulphide was evolved; the mixture was poured into water and the precipitate crystallised from alcohol. It consisted of carvone hydrosulphide (m. p. 214°; nitrogen test negative) and a small quantity of carvoxime (m. p. 72°).^{*} On passing hydrogen sulphide into an ammoniacal alcoholic solution of carvoxime, a small quantity of carvone hydrosulphide and much unchanged oxime were obtained.

When the hydrosulphide was heated at 100° for several hours with a concentrated solution of sodium hydrogen sulphite, it was unchanged.

Action of Mercuric Chloride and Other Reagents on Carvone Hydrosulphide.—The hydrosulphide in chloroform was treated with an

^{*} Duplobenzylideneacetone mono- and di-sulphides are converted by phenylhydrazine into benzylideneacetonephenylhydrazone and hydrogen sulphide (Fromm, *Annalen*, 1914, **394**, 300).

etheral solution of mercuric chloride. A yellow solid was precipitated which was free from organic matter and with sulphuric and hydrochloric acids gave hydrogen chloride and hydrogen sulphide, respectively, and was probably the double compound $2\text{HgS}\cdot\text{HgCl}_2$.* The filtrate gave an oil which appeared to be carvone, but was not further examined.

The hydrosulphide is unchanged after several hours' contact with cold acetic anhydride. With glacial acetic acid, some hydrogen sulphide is slowly evolved, but the bulk of the product is not altered after several days.

Thiocyanogen and Triphenylstibine.—Triphenylstibine (5 grams) was dissolved in 72 c.c. of a solution prepared from 7.5 grams of lead thiocyanate, 3 grams of bromine, and 100 c.c. of dry ether. After five hours, light petroleum was added, when white crystals (m. p. 100°) were deposited. On recrystallisation from alcohol, these melted at $105\text{--}106^\circ$ (Found: N = 5.76, 5.86, 6.18; S = 13.63, 13.95.† $\text{C}_{20}\text{H}_{15}\text{N}_2\text{S}_2\text{Sb}$ requires N = 5.99; S = 13.66 per cent.). The ethereal solution yielded only polymerised thiocyanogen and some unchanged stibine.

Triphenylstibine dithiocyanate forms broad, white needles which dissolve easily in most organic solvents except light petroleum. When heated at about 250° , it decomposes, giving an odour of phenyl thiocyanate.

Triphenylstibine Dichloride and Lead Thiocyanate.—The dichloride (5.8 grams) was shaken with 44 grams of lead thiocyanate and 30 c.c. of dry benzene for eight hours, the solid separated, and washed with dry benzene and cold acetone. The filtrate was treated with light petroleum, yielding a white solid, m. p. $221\text{--}225^\circ$. On recrystallisation from benzene and light petroleum, this melted at $227\text{--}228^\circ$ (Found: N = 2.90; S = 7.81. $\text{C}_{19}\text{H}_{15}\text{ONSSb}$ requires N = 3.28; S = 7.51 per cent.).

Triphenylstibine hydroxythiocyanate is readily soluble in most organic solvents except light petroleum. With excess of an ethereal solution of thiocyanic acid, it yields the dithiocyanate.

The original benzene solution was concentrated slightly and treated with more light petroleum, when three crops of crystals, m. p. 105° , were obtained. These were free from halogen and on recrystallisation did not depress the m. p. of triphenylstibine

* The thiodigalactose which is obtained by the interaction of acetyl bromide-galactose and potassium sulphide and subsequent hydrolysis with methylalcoholic ammonia, and contains the grouping $-\text{S}-$, yields this compound with mercuric chloride (Schneider and Deuther, *B. z.*, 1919, 52, 2148).

† Some of these analyses were performed with the product obtained from the dichloride and lead thiocyanate (above). The sulphur was estimated by the Carius method, the precipitated antimonious acid being carefully separated.

dithiocyanate (105—106°) obtained by means of thiocyanogen (p. 1052). When the dithiocyanate was boiled with water for eight hours, the aqueous liquor contained thiocyanic acid. The solid (m. p. 225°) on recrystallisation from acetone and light petroleum melted at 228° and did not depress the m. p. of triphenylstibine hydroxythiocyanate.

A product containing sulphur and melting at 221°, which was almost certainly the hydroxythiocyanate, was isolated from the reaction of triphenylstibine hydroxychloride and lead thiocyanate in cold dry benzene. The quantity was insufficient for further purification.

Thiocyanogen and Triphenylarsine.—Triphenylarsine (8 grams) was dissolved in 130 c.c. of a solution of thiocyanogen (2 mols.) prepared from 11.25 grams of lead thiocyanate, 4.5 grams of bromine, and 150 c.c. of dry ether. A pale yellow solid (m. p. 91°; 5 grams) was deposited. On extraction with benzene, precipitation with ether, and crystallisation from a mixture of acetone and light petroleum, polymerised thiocyanogen was removed and colourless crystals were finally obtained, m. p. 110° (decomp.) (Found: N = 3.37; S = 8.32, 8.62. $C_{19}H_{15}ONSAs$ requires N = 3.67; S = 8.39 per cent.).

Triphenylarsine hydroxythiocyanate dissolves readily in most organic solvents except light petroleum. It instantly reacts with warm alcoholic silver nitrate, giving silver thiocyanate. At its m. p., it decomposes vigorously, evolving ammonia and an odour of phenyl thiocyanate. On further heating, a liquid distils which solidifies on cooling and crystallises from alcohol in long, glistening needles which melt at 162° and do not depress the m. p. of triphenylarsine sulphide (Philips, *Ber.*, 1886, **19**, 1032). Traces of this substance were also found in the mother-liquors obtained on repeated crystallisation of the hydroxythiocyanate.

Triphenylarsine Dichloride and Lead Thiocyanate.—The dichloride (2 grams, 1 mol.) and lead thiocyanate (2.5 grams, 1.5 mols.) were shaken with 25 c.c. of dry benzene. The mixture rapidly became red, a brown oil, which became a crystalline solid, being deposited. After forty minutes, this was separated and washed with light petroleum. The residue (3.4 grams) was extracted with acetone, which finally deposited colourless crystals, m. p. 110°, which did not depress the m. p. of triphenylarsine hydroxythiocyanate (above). About 0.15 gram of triphenylarsine, m. p. 56—60°, * was obtained from the petroleum washings and the original benzene solution.

* This small amount of arsine may possibly have been present in the original dichloride which, owing to its hygroscopic nature and tendency to form the hydroxychloride, was not recrystallised. Pure specimens of tri-

Triphenylarsine Hydroxychloride and Lead Thiocyanate.—The hydroxychloride (m. p. 171° ; 4 grams) was shaken for thirteen hours with excess of lead thiocyanate and benzene, a pink colour being at once produced. The mixture was then filtered. The residue on extraction with acetone gave a deep red solution which, with light petroleum, deposited (a) a small amount of a yellow substance of high m. p. and (b) white crystals, m. p. 110° after recrystallisation from acetone–light petroleum. These did not depress the m. p. of triphenylarsine hydroxythiocyanate prepared from thiocyanogen (p. 1053).

The benzene filtrate, when treated with light petroleum, deposited a solid (m. p. $148\text{--}149^{\circ}$) containing sulphur and nitrogen but no halogen. On recrystallisation, this behaved as a mixture, but no definite compound could be isolated.

Thiocyanic Acid and Triphenylbismuthine.—When the bismuthine (4.4 grams) was treated with thiocyanic acid (about 2.5 grams) in ether (20 c.c.), it gradually dissolved. An oil was deposited (1.4 grams) which quickly crystallised, melted sharply at 123.5° , did not depress the m. p. of diphenylthiocyanobismuthine, and possessed all the properties of this substance. After five days, the filtrate deposited 1.2 grams of a yellow, crystalline solid which became red at 176° and melted at $185\text{--}186^{\circ}$. This was insoluble in benzene or ether, and appeared to be decomposed by hot alcohol or acetone. It probably consisted of phenyldithiocyanobismuthine. With concentrated hydrochloric acid, it evolved benzene, indicating the presence of a phenyl derivative of tervalent bismuth. No phenyl thiocyanate was isolated, and even its odour could not be detected with certainty. Only traces could possibly have been present.

Action of Thiocyanic Acid and of Thiocyanogen on Triphenylphosphine.—Two grams of the phosphine were dissolved in 20 c.c. of an ethereal solution containing about 2.5 grams of thiocyanic acid. After about a month, the ether was removed at the ordinary temperature, and the solid residue drained on a tile and crystallised from alcohol. Some unchanged phosphine was recovered, but the mother-liquors yielded colourless needles which contained sulphur but no nitrogen and melted at 158° . They did not depress the m. p. of a specimen of triphenylphosphine sulphide or of the product obtained by the use of thiocyanogen (see below). No phenyl thiocyanate was produced.

triphenylarsine dichloride are stated to sinter at 158° and melt at $204\text{--}205^{\circ}$. Our specimen exhibited this property and was considered sufficiently pure, the sintering being at first attributed to the onset of decomposition to chlorobenzene and diphenylchloroarsine, which is known to occur at 300° (Michaels, *Annalen*, 1902, **321**, 162; Rosenheim and Bilecki, *Ber.*, 1913, **46**, 551).

In the reaction with thiocyanogen 3 grams of the phosphine in 20 c.c. of dry ether were treated with 92 c.c. of a similar solution containing 2.8 grams (2.2 mols.) of thiocyanogen. A red oil, which soon solidified, was immediately precipitated, followed almost at once by the usual yellow polymeride, which, however, was produced much sooner than in any other reaction we have studied. The viscous solid was separated and repeatedly extracted with cold dry benzene and the combined extracts were evaporated in a stream of dry carbon dioxide. The residue was triphenylphosphine sulphide, and a further quantity was obtained by similar treatment of the filtered ethereal solution.

Interaction of Thiocyanogen and Thiocyanic Acid with Other Unsaturated Compounds.

Thiocyanogen.—Amylene (trimethylethylene) in ethereal solution gives an oil which is volatile with steam. This is a thiocyanate, since with alcoholic potassium hydrosulphide a mercaptan and potassium thiocyanate are produced. Benzylideneacetone readily yields a yellow, crystalline, saturated substance, m. p. 118–120°, containing nitrogen and sulphur. Carvone and ethyl cinnamate give extremely poor yields of well-crystallised compounds, m. p. 254° and 153°, both containing nitrogen and sulphur.

Thiocyanic Acid.—*l*-Pinene reacts with an ethereal solution of thiocyanic acid, giving a substance, m. p. 92°, containing nitrogen and sulphur. The investigation of these compounds is being continued.

Most of the expenses of this investigation have been defrayed by a grant from the Research Fund Committee of the Chemical Society, for which the authors desire to express their thanks.

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[Received, March 14th, 1923.]

CXX.—*Studies on the Dolomite System. Part I.*
The Nature of Dolomite.

By ALLAN ERNEST MITCHELL.

DOLOMITE has always been regarded by mineralogists as a compound of the composition $\text{CaCO}_3 \cdot \text{MgCO}_3$, but some doubt as to the accuracy of this view has been expressed by Spangenberg (*Z. Krist. Min.*, 1914, 52, 529), who, from the results of his investig-

ations on its synthesis, puts forward the idea that dolomite is not necessarily a compound, but is a solid solution of calcite and magnesite. He places the limits of miscibility between the proportions $\text{CaCO}_3, 2\text{MgCO}_3$ and $\text{MgCO}_3, 2\text{CaCO}_3$, so that normal dolomite would be an equimolecular solid solution, and any naturally occurring dolomites departing appreciably from this proportion would be due to changes in the composition and not necessarily to admixture of accidental impurities. The substances prepared by him, however, have physical properties which do not correspond with normal dolomite and his results in general leave much doubt as to the actual nature of the products he obtained; it seems more than probable that his substances were mixtures of vaterite (modification of calcite plus immeshed aragonite) and magnesite, or aragonite and magnesite. It is necessary, therefore, that some investigation of the actual individuality of dolomite should be made.

If we consider the analyses of various samples of dolomite from different parts of the world (Doelter, "Handbuch der Mineral-chemie," Bd. 1, 364, etc.), we shall readily see that so far as the natural product is concerned it does not depart appreciably from equimolecular proportions. Dolomite occurs in various parts of the world under different conditions, and it seems very hard to imagine that if the formation is one of solid solution the practically equimolecular mixture would occur in every case, unless the miscibility is only very limited, and certainly not as wide as that asserted by Spangenberg.

In order to get an idea as to the individuality of the substance, it became necessary first of all to determine its relative stability with respect to the other two members of the rhombohedral carbonates, calcite and magnesite, and since by the application of the Nernst heat theorem we are able to get a fairly accurate statement of the connexion between heat of formation, temperature, and dissociation pressure of a compound, the most fruitful line of attack seemed to be in a comparison of the thermal dissociation pressures of the three substances. In order, then, that these dissociation pressure relationships could be correlated, it was essential that we should have a knowledge of the specific heats and the heats of formation of all the reactants involved, and this necessitated the determination of the specific heats of magnesite and of the decomposition product of dolomite, and the heats of formation of dolomite and of its decomposition product.

Kallauner (*Chem. Ztg.*, 1913, **37**, 1317), who has made measurements of the thermal dissociation of dolomite, concludes that the substance is split into its components, calcium carbonate and

magnesium carbonate, at 500°. The degree of this decomposition reaches a maximum at 700°, the liberated magnesium carbonate dissociating to give carbon dioxide. Dissociation of the residual calcium carbonate begins at 875° and reaches a maximum at 900°.

Johnston (*J. Amer. Chem. Soc.*, 1910, **32**, 933) has made measurements of the thermal dissociation of calcite, and has shown from his measurements that the relationship between dissociation pressure and temperature is represented by the equation

$$\log p = -9340/T + 1.1 \log T - 0.0012 T + 8.882,$$

where p = pressure in atmospheres and T = absolute temperature.

EXPERIMENTAL.

The materials required for these investigations offered some considerable difficulties owing to the necessity of employing natural magnesite and dolomite. Calcite can be easily prepared in the laboratory and the ordinary analytical reagent is sufficiently pure for the purpose. The supply of the other two is rendered difficult owing to natural conditions, since it is practically impossible to obtain natural minerals which are free of iron oxides and silica. After a search which necessitated an examination of samples from various parts of the world, two separate samples of dolomite were obtained which were of sufficient purity. These were respectively from Algeria and Binnental (Switzerland). Although they were not pure, they were the best that could be hoped for from a natural product. Their analyses are given below.

The only sufficiently pure magnesite obtainable was a sample of clear, colourless, rhombohedral mineral from the Greiner region of the Tyrol. Owing to the fact that it occurred in a chlorite schist it was very hard to get it free from iron oxide, but after careful hand-picking under a microscope a suitable sample was obtained.

	CaO.	MgO.	FeO.	SiO ₂ .
Algerian dolomite	30.31	21.61	0.75	0.10
Binnental dolomite	30.89	21.21	trace	trace
Normal dolomite	30.45	21.72	—	—
Greiner magnesite (hand-picked) ..	2.32	43.84	1.87	0.50

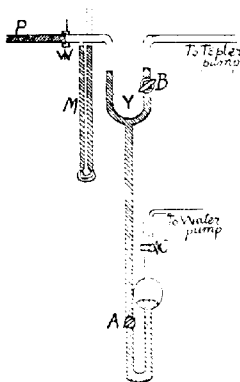
The samples for treatment were crushed to pass a 20-mesh sieve, and then hand-picked under a microscope until no fragments containing visible inclusions were left. The balance was crushed in an agate mortar until it passed a 120-mesh sieve.

Preliminary investigations were made in which the carbonate, enclosed in a platinum capsule, was heated in a transparent silica tube connected by stout rubber pressure tubing to a mercury manometer. The system was evacuated and the carbonate heated

by placing the silica tube in an electric furnace, but it was found to be impossible to obtain reproducible results. This was found to be due to (1) leakage through the rubber connecting tube. This was at the most very small and by no means so great as (2) leakage through the silica tube due to devitrification induced by the reaction of the silica and small traces of the carbonates which always escaped from the platinum no matter how carefully the tube was exhausted. The crystalline silicates formed on the surface of the silica glass by this reaction appear to have served as nuclei for the formation of quartz crystals, as was shown by microscopical examination of the tubes.

The apparatus ultimately employed is shown in Fig. 1.

FIG. 1.



The platinum tube *P*, 15 cm. long by 0.5 cm. internal diameter with thickness of wall 0.5 mm., was sealed directly to the glass manometer *M*, the joint if carrying a cooling coil to prevent cracking of the joint by heating from within the furnace. The tube was exhausted through the trap *Y* and the mercury allowed to rise from the lower bulb. Then, when *A* and *B* were closed, the mercury in the trap was so held that it could not be pushed round the bend when a pressure was developed. The substance to be heated was placed in the tube *P*, the open end of which was packed with asbestos dehydrated at about 800°, and the platinum tube then sealed on to the glass, and the electric furnace so arranged that the carbonate was well

within the zone of constant temperature. The tube was heated to about 200–300° in order to free the powder from adsorbed moisture and gases, and the exhaustion completed. The temperature, which was read by means of a carefully calibrated platinum-platinum-rhodium thermo-couple, was raised until an appreciable pressure was developed. On re-exhausting the tube at this temperature and then allowing the pressure to rise again, it was found that it did not return to its original value, but was always less. On repeating this process several times, a constant minimum pressure could be obtained for every temperature. The gas evolved under these conditions was collected, and analysis showed it to consist entirely of carbon dioxide. Micro-

scopical examination of the decomposition product showed the existence of a small amount of needle-shaped crystals which were not present in the sample before heating. These were insoluble in alkalis or water, but gelatinised very readily with acids, giving microchemical tests for calcium and magnesium; these properties in conjunction with the optical properties identify the crystals as calcium and magnesium silicates formed by the interaction of the carbonates with the small traces of siliceous impurities, so that the initial high pressures of carbon dioxide must have been due to the reaction $\text{CaCO}_3 + \text{SiO}_2 \rightarrow \text{CaSiO}_3 + \text{CO}_2$, etc. These reactions may be regarded as irreversible at the temperatures under discussion, and although it would be possible for further carbonate and silicate to react, giving further complex silicates, there will always be a time when the combination with silica comes to an end for every temperature, and the dissociation pressure of the carbonate will then be unaffected by the presence of the silica. The resultant constant minimum pressure for any temperature was therefore taken as the dissociation pressure of the carbonate for that temperature. The time taken for the establishment of the equilibria under these conditions was considerable in the case of the lower temperatures, but equilibrium was obtained much more rapidly the higher the temperature, and usually resulted within forty-eight hours of the initial evacuation at any temperature. Having established a method for obtaining reproducible results with rising temperature, it became necessary to test the reversibility of the process, and it was found that when equilibrium was attained at a higher temperature, which was then allowed to fall to a lower value, the equilibrium pressure for that temperature was not obtained, even after keeping the temperature constant for forty-eight hours. There was always some residual carbon dioxide which apparently would not recombine. This fact is referred to by Jolibois and Bouvier (*Compt. rend.*, 1921, **172**, 1182), who found that the reaction $\text{CaO} + \text{CO}_2 \rightarrow \text{CaCO}_3$ was not reversible unless the calcium oxide used was previously mixed with some calcium carbonate, prepared by a precipitation method, when the reaction was completely reversible on cooling.

The procedure was then adopted in which the carbonates under treatment were mixed with their appropriate oxides, prepared by ignition of the precipitated hydroxides, or in the case of the dolomite by ignition of the moistened product of the decomposition. When this was done, it was found that with rising temperature the results obtained were the same as before, and that with falling temperature the reaction was completely reversible, the pressures checking to a fraction of a millimetre. It was found necessary,

however, to recharge the tubes frequently, since the reversibility would only hold for a few temperatures until further oxide was introduced. Thus it seems that we have an explanation of this phenomenon in the idea that a trace of moisture serves to catalyse the reaction. Carbonates and oxides prepared by precipitation methods will always contain small traces of moisture no matter how carefully they are afterwards ignited. This small trace of moisture would be easily sufficient to catalyse the reaction, but it will be slowly removed by the pumping off of the gas at each temperature, and would thus require renewal from time to time.

TABLE I.

Calcite.

T° (abs.)	876°	890°	903°	915°	929°	942°	954°	967°
Pressure (mm. of Hg)	2.4	2.5	2.6	2.7	2.9	3.0	3.2	3.4
T° (abs.)	980°	993°	1006°	1019°	1032°	1045°	1059°	1071°
Pressure (mm. of Hg)	3.6	3.9	4.2	4.7	5.2	5.9	6.9	8.1
T° (abs.)	1084°	1097°	1109°	1123°	1135°	1148°	1161°	1166°
Pressure (mm. of Hg)	10.0	13.0	17.8	27	46.5	100.0	316.2	616.6

Magnesite.

T° (abs.)	720°	730°	740°	750°	760°	770°	780°	790°
Pressure (mm. of Hg)	10.5	11	11.6	12.2	12.9	13.7	14.6	15.5
T° (abs.)	800°	810°	820°	830°	840°	850°	860°	870°
Pressure (mm. of Hg)	16.6	18.1	19.5	21.1	23	25	27.5	31.1
T° (abs.)	880°	910°	950°	980°	1000°	1020°	1029°	
Pressure (mm. of Hg)	34.6	49.6	61.2	117	316.5	602.5	760	

Dolomite.

T° (abs.)	780°	785°	793°	810°	820°	830°	846°	855°
Pressure (mm. of Hg)	7.5	7.7	8.0	8.7	9.0	9.6	10.0	12.8
T° (abs.)	896°	910°	920°	936°	940°	960°	970°	982°
Pressure (mm. of Hg)	14.6	16.5	17.8	21.0	22	27.5	29.5	32.5
T° (abs.)	995°	1010°	1020°	1030°	1042°	1052°	1060°	1065°
Pressure (mm. of Hg)	13.6	53.0	66.0	77	100.0	121	150	193
T° (abs.)	1070°	1080°	1085°	1089°	1092°	1095°	1100°	1105°
Pressure (mm. of Hg)	212.7	275	352	368	468	505	603	695

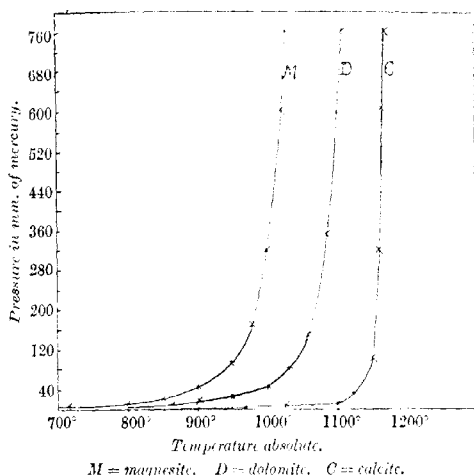
Determinations of the dissociation pressures of calcite, magnesite, and dolomite have been made by means of this method and the results are given in Table I. Fig. 2 shows the variation of pressure with temperature, and if these curves are tested by plotting $1 \log p$ against T , it will be found that they express a definite linear relationship between the reciprocal of the logarithm of the pressure and the temperature.

The Specific Heat of Magnesite.

This was determined in the following manner. As calorimeter, a small Dewar vessel of about 500 c.c. capacity and of very good

insulation was employed. This was fitted with a Beckmann thermometer, stirrer, and small heating coil of carefully measured known resistance. The vessel was partly filled with carbon tetrachloride so that the thermometer was correctly situated. A steady known current, which was carefully checked by means of a silver coulometer in series, was passed for a definite time, the rise of temperature measured, and the corresponding amount of heat added was calculated from the ordinary expression $Q = C^2Rt \times 0.2349$. Without changing the contents in any way, a known weight of dry magnesite was added and the same current passed for the

FIG. 2.



same time as before and the new rise in temperature determined. The amount of heat added, and the rise of temperature both with and without a known weight of the sample, being known, it is possible to calculate the amount of heat used up in heating the magnesite. In one experiment, which represents the smallest quantities employed, the following were the figures :

$C = 0.085$, $R = 34.7$, $t = 600$ secs., whence $Q = 44.15$ cals.

Rise in temperature = 0.553° (without magnesite) and 0.548° (with magnesite, 5.7114 grams).

Therefore heat for magnesite = $44.15 - 44.15 \times 0.548 / 0.553 = 0.63$ cal., and its specific heat = 0.2013 cal.

Several determinations were made in this manner, employing

0.0*

different amounts of liquid, solid, and current until the largest changes could be obtained. The results were fairly concordant and were sufficiently accurate to be used along with the other data employed in the approximate formula for the Nernst equation. The results obtained were: (1) 0.2013, (2) 0.1997, (3) 0.2007, (4) 0.1995; mean 0.2003 cal.

These determinations were made on a sample of Greiner magnesite which, although it was not absolutely pure, was sufficiently so for the purpose in view.

*The Specific Heat of CaO, MgO .**

A sample of finely ground Binnental dolomite was heated in a vacuum at 1000° until its weight was constant and was then cooled in a desiccator over solid potassium hydroxide to prevent any reabsorption of carbon dioxide. The substance was not very reactive, however, and it was found possible to leave it exposed to the air for considerable periods when cold without any pronounced alteration taking place. The specific heat of this product, determined as above, was (1) 0.2100, (2) 0.2110, (3) 0.2093, (4) 0.2096, (5) 0.2106; mean 0.2101 cal.

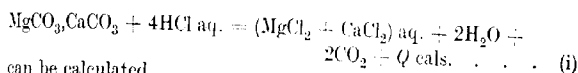
The Heat of Solution of Dolomite.

The heat of formation of this substance has never been determined either from its elements or in any other manner, and it became necessary to determine the value both for dolomite itself and for the decomposition product. When either dolomite or the decomposition product is dissolved in hydrochloric acid, the only possible products of the reaction are calcium and magnesium chlorides, water, and carbon dioxide. The heats of formation of these four substances have all been determined previously, and Berthelot has made careful determinations of the heat of dilution of hydrochloric acid over a fairly wide range, so that we have only one unknown in either equation for the reaction with acid.

The apparatus employed was similar to that used by Richards in his early measurements. The calorimeter consisted of a large Dewar vessel of about $1\frac{1}{2}$ litres capacity and of very good insulation. This was closed at the top by a cork carrying a Beckmann thermometer, a stirrer, a large cylindrical vessel closed at the bottom by a large ground glass plug which could be withdrawn by means of a protruding rod at the top, and two tubes, into the lower ends of which were sealed the ends of the small platinum heating spiral, and the whole was placed in a large box packed with cotton wool

* The formula CaO, MgO will be used for the sake of brevity to denote the decomposition product of dolomite.

to provide further insulation. The bottom of the internal vessel was carefully sealed by liberal application of purified vaseline to the ground plug. In this vessel were placed 200 c.c. of pure 20 per cent. hydrochloric acid, prepared by distillation of ordinary hydrochloric acid. A known weight of dolomite less than that required to neutralise the acid completely was placed in the bottom of the calorimeter and the total volume of liquid made up to a litre with 800 c.c. of distilled water. The dolomite was kept in suspension by means of the stirrer, and the thermal capacity of the calorimeter and fittings determined both by the electrical method and the method of mixing, allowance being made for the thermal capacity of the dolomite. This determination was made both before and after the reaction and was found to be constant within the limits of error throughout. Then, when the plug of the internal vessel was withdrawn, the acid could be allowed to react with the carbonate and the rise in temperature determined. By making corrections for the heat of dilution of the acid and the amount of heat lost in the evolution of carbon dioxide (which amount was found in the end to be negligible, since at the concentrations employed most of the carbon dioxide remained in solution and very little was lost), the heat given out in the reaction



can be calculated.

In the preliminary experiments, since it was anticipated that the loss of heat due to evolution of carbon dioxide would be considerable, two calorimeters were employed which were connected by a double-walled tube, silvered, and exhausted so as to form a Dewar jacket. This tube, which was bent twice at right angles, dipped under the surface of water in the second calorimeter, and thus by measuring the rise of temperature in the second calorimeter it was possible to obtain accurate measurement of the heat carried away by the issuing carbon dioxide. This amount of heat was in all cases negligible, never amounting to as much as 0.02 per cent. of the total amount developed, and it was soon apparent that attempts to increase the accuracy in this respect were largely counterbalanced by the inaccuracies introduced by the necessity of having to attend to two calorimeters and to read two Beckmann thermometers simultaneously. The only fault in this apparatus was that the size of the opening of the internal vessel could not be made sufficiently large owing to the presence of the other fittings, and consequently the mixing was not quite rapid enough. The Dewar vessel had very good insulation, however, and since the

radiation corrections could be reduced practically to zero this was not after all a serious defect in the working of the apparatus.

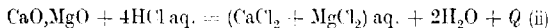
In an actual experiment the results were:

Weight of dolomite = 0.6766 gram; temperature rise = 1.81° ; total thermal capacity of calorimeter = 303 grams; acid diluted from 1.33:10.7 to 1.33:52.8 mols. For this range the heat of dilution is 1198 cal. (Berthelot, Landolt-Bornstein "Tabellen"). The total heat developed = 2353 cal. Therefore the heat of reaction = 1155 cal. for 0.6766 gram, that is, 31.42 Cals. for 1 gram-molecule.

Several determinations were made using different amounts of dolomite and acid, and the results, which are fairly concordant amongst themselves, are: (1) 31.52, (2) 31.32, (3) 31.26, (4) 32.02, (5) 31.68; mean 31.56 Cals., which is the value of Q in equation (i).

The Heat of Solution of CaO, MgO in Hydrochloric Acid.

To determine the value of Q in the equation



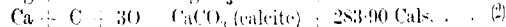
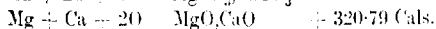
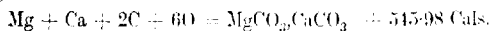
it was necessary to determine the heat of solution of this substance; from this value, by incorporating the known values for the heats of formation of the other reactants, it was possible to determine the heat of formation of the substance from its elements.

The apparatus employed was essentially the same as that already described, except that in this case, since we are dealing with a substance tending to undergo hydration on mixing with water, the oxide was placed in the internal vessel, which was made smaller, and the acid occupied the position of the water in the preceding determinations.

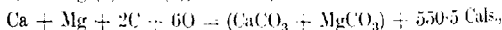
Several determinations of the heat of solution were made and the results are: (1) 62.82, (2) 62.75, (3) 62.90, (4) 63.15, (5) 62.53; mean 62.83 Cals., which is the value of Q in equation (ii).

Discussion.

From equation (i) and the figures of Thomsen and Berthelot given in Landolt-Bornstein "Tabellen" we have



whence, adding (1) and (2), we have,

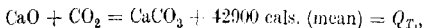


which leaves a balance of only 4.52 Cals. to account for the heat of formation of dolomite from calcite and magnesite.

If we now consider the Nernst equation for a heterogeneous reaction in which only one gas is formed, we have

$$\log p = \frac{-Q_{T_1}}{2.3RT} + \frac{3.5}{R} \left(\log T + \frac{T_1}{2.3T} \right) - \frac{\Sigma a}{2.3 \times 2R} \left(T + \frac{T_1^2}{T} \right) + c.$$

Taking $T_1 = 300^\circ$ abs., we have, according to Thomsen and De Forerand (Landolt-Börnstein "Tabellen"),



also at 300° abs.,

$$c_{\text{CaO}} - c_{\text{CO}_2} - c_{\text{CaCO}_3} = 20.2 - 10.2 = 9.0,$$

whence

$$\Sigma a = 0.0153.$$

Substituting in the first equation, we have finally

$$\log p = -9160/T + 1.75 \log T - 0.00177T + 3.2,$$

where c = chemical constant for carbon dioxide = 3.2 (Nernst).

For $T = 1006^\circ$ abs.,

$$\log p = -2.4 \text{ or } p = 0.004 \text{ atm.} = 3.0 \text{ mm.}$$

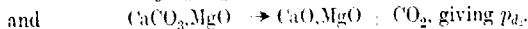
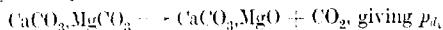
Johnston (*loc. cit.*) obtained $p = 44$ mm.; in the present observations, we found $p = 4.2$ mm. at 1006° abs.

The equation given by Johnston departs very appreciably from the form derived directly from the Nernst equation, but the other values measured in this work agree much more closely with the Nernst expression, and when they are plotted do not depart appreciably from the calculated results, so that it seems unnecessary to modify the expression in order to make it fit the observed facts. The specific heat data are evidently quite accurate for this reaction. In the case of the magnesite and dolomite, the agreement between the observed results and those calculated from the Nernst equation is not so good, but the departure from the theoretical does not warrant the derivation of a special equation which would be of no physical significance. The curves are so decidedly logarithmic in form that it does not seem possible that they can represent any but the true state of affairs. The disagreements may possibly be due to the slight inaccuracies in the specific heat data or, what is more probable, they can be traced to the calcareous and ferruginous impurities in the samples used, which, it must be borne in mind, were natural products and not entirely free from impurity.

In dealing with the thermal dissociation of dolomite, we have to consider two possibilities, namely, that dolomite is either a compound or a solid solution. Assuming first that it is a compound, it is possible to conceive of the following as the products of its dissociation under the action of heat: (1) $\text{CaO}, \text{MgCO}_3 + \text{CO}_2$, (2) $\text{CaCO}_3, \text{MgO} + \text{CO}_2$, (3) $\text{CaO}, \text{MgO} + 2\text{CO}_2$, (4) $\text{CaCO}_3 + \text{MgO} + \text{CO}_2$, (5) $\text{CaO} + \text{MgCO}_3 + \text{CO}_2$, (6) $\text{CaO} + \text{MgO} + 2\text{CO}_2$.

Now, in the experimental work described, it has been shown that magnesite, dolomite, and calcite all yield definite dissociation pressures, p_m, p_d, p_c such that $p_m > p_d > p_c$. These results at once rule out the possibility of such reactions as (5) and (6), since calcium oxide cannot exist as a solid phase at pressures of carbon dioxide greater than p_c , and also calcium oxide and magnesia cannot coexist at the same pressure of carbon dioxide.

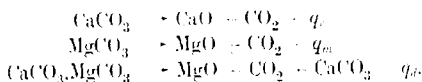
On the assumption that dolomite has a second dissociation pressure, the reaction must be either (1) or (2), the latter being the more probable. Thus we should have a case somewhat similar to that of the ionisation of a dibasic acid or a diacidic base. Dolomite would show two definite and successive dissociation pressures, p_d and p_d' , corresponding with the two successive reactions



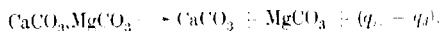
It is to be noted that the second possibility could not be represented by $\text{CaCO}_3 \cdot \text{MgO} \rightarrow \text{CaO} + \text{MgO} + \text{CO}_2$, because it is impossible for calcium oxide and magnesia to coexist at the same pressure of carbon dioxide.

If the assumption of a second dissociation were correct, it would have been possible to isolate the basic carbonate and the double oxide. Dolomite, however, does not show a second dissociation pressure over the temperature range examined, and therefore reactions (1) and (2) are excluded.

If assumption (4) were correct, the curves showing the relationships between p_c , p_d , and p , would give us the energy changes of the reactions:



from which it would follow that



$$\text{where } q_c - q_d = RT^2 \log \frac{d}{dt} \log \frac{p_m}{p_d},$$

although this value would in any case tend to be very small, even if it existed at all.

The corresponding diminution of free energy would be given by the expression

$$-F = F_d - (F_c + F_m) = RT \log \frac{p_d}{p_m},$$

but since from the observations at the temperature range at command we have $p_m > p_d$, then $F_c + F_m > F_d$, and therefore the

reaction $\text{CaCO}_3, \text{MgCO}_3 \rightarrow \text{CaCO}_3 + \text{MgCO}_3$ should occur or, in other words, dolomite would be unstable with respect to the component simple carbonates and should not be capable of being formed from them. This result is indeed obvious, for if the condensed reaction $\text{CaCO}_3, \text{MgCO}_3 \rightarrow \text{CaCO}_3 + \text{MgCO}_3$ actually did occur, dolomite would show the same dissociation pressure as magnesite in its first dissociation phase, provided, of course, that no solid solutions whatsoever are formed during the process. Hence from the observed results the reaction cannot be (4), and we can only draw the conclusion that, if the substance be a compound, its mode of dissociation must be (3), for examination of the $1/\log p$ curves for the temperature range shows conclusively that there is not a second dissociation phase.

If we now consider the second possibility that dolomite might be a singular point in a series of solid solutions, we should expect results analogous to those obtained.* There would be a definite dissociation pressure curve and the resulting product would be an equimolecular solid solution of calcium oxide and magnesia. It has been shown by Rankin and Merwin (*J. Amer. Chem. Soc.*, 1916, 38, 568) that in fused mixtures of these two oxides no compounds or solid solutions are to be found. These results were all obtained at temperatures higher than 2300°, the melting point of the eutectic, but there does not seem any theoretical reason why it should not be possible for either solid solutions or compounds to exist at the temperatures at which the present measurements were made.

The very small value obtained for the heat of formation of dolomite from magnesite and calcite might possibly not be worthy of consideration, because it only involves the absorption of 4.52 kg.-cals. in the formation of one gram-molecule, or about 24.8 cals. per gram. The accuracy of the measurements involved and of the thermochemical data accepted would not allow of too much stress being laid upon this difference. It might be worth while considering, however, whether this amount of heat could represent merely the heat of solution of a gram-molecule of calcite in a gram-molecule of magnesite or whether the heat is actual heat of chemical combination. We know that when two substances of the type here considered unite to form a double compound its heat of formation is as a rule, although not always, only very slightly different from the sum of the heats of formation of the two combining molecules, and also that the heat of solution of similar substances one in the other is usually very small and can possibly be negative, so that it appears to be impossible from the evidence at hand to decide whether the substance is a solid solution or a compound. Experiments are in progress which it is hoped will enable us to decide the

limits of possible miscibility of the two simple carbonates, and this information in conjunction with the results of investigations which the author hopes to make on the dissociation of some series of mixed crystals should ultimately allow us to come to a definite decision upon the matter. Most of the evidence adduced, however, points to the existence of a compound of the two carbonates, and it seems more useful, for the present at least, to regard the old and original idea of the constitution of dolomite as correct, unless we can come to a decision as to the essential difference between a definite chemical compound and an equally definite singular point in any series of solid solutions.

Summary.

(1) Measurements of the dissociation pressures of calcite, magnesite, and dolomite have been made and it has been shown that the three substances yield three different and definite dissociation pressures p_c , p_d , p_m such that $p_m > p_d > p_c$. The possible modes of dissociation of dolomite have been considered on the ground that it is a compound and from the results it is concluded that the thermal dissociation of dolomite takes place according to the equation $\text{CaCO}_3 \cdot \text{MgCO}_3 \rightleftharpoons \text{CaO} \cdot \text{MgO} + 2\text{CO}_2$.

(2) It has been shown that the thermal dissociation of calcite follows the Nernst equation, the agreement between the observed and calculated results being good, so that the necessity for the derivation of a particular equation to fit the case, as has been done by Johnston, has been proved unnecessary.

(3) A simple and fairly accurate apparatus for the determination of specific heats of solids has been described, and has been employed for the determination of the specific heats of magnesite and of the solid decomposition product of dolomite, which have been found to be 0.2003 and 0.2101 cal., respectively, for 15–20°.

(4) The heats of solution of dolomite and of its solid decomposition product in hydrochloric acid have been determined, and from these measurements the heats of formation of the two substances from their elements have been calculated.

(5) From these determinations, it has been deduced that the formation of dolomite from magnesite and calcite would involve the absorption of 4.52 kg.-cals. per gram-molecule of dolomite. It has been pointed out that with our present knowledge it is impossible to decide definitely whether the substance is a singular point in a series of solid solutions, or whether it is a compound.

In conclusion, the author takes this opportunity of thanking Prof. F. G. Donnan, F.R.S., for suggesting this research, and for

his kind interest and many valuable suggestions during the progress of the work, and also Dr. A. Hutchinson, F.R.S., of the University of Cambridge, for his kindness in providing a sample of very pure dolomite at a critical time.

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[Received, March 6th, 1923.]

CXXI.—*The Oxime of Mesoxamide (iso-Nitrosomalondimethyl-anilide) and some Allied Compounds. Part III. Ring Formation in the Tetra-substituted Series.*

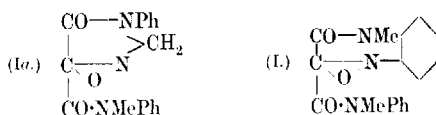
By EDITH HILDA USHERWOOD and MARTHA ANNIE WHITELEY.

IN the course of the preparation of *isonitrosomalondimethylanilide*,

$(\text{NMePh}\cdot\text{CO})_2\text{C}\begin{smallmatrix} \text{NH} \\ \diagup \diagdown \\ \text{O} \end{smallmatrix}$, by the action of nitrosyl chloride on malon-

dimethylanilide it was observed that the presence of moisture caused simultaneous hydrolysis and oxidation of the compound, yielding a mixture of *mesoxdimethylanilide*, $(\text{NMePh}\cdot\text{CO})_2\text{CO}$, and a compound, m. p. 191° , having the molecular formula $\text{C}_{17}\text{H}_{15}\text{O}_3\text{N}_3$ (Whiteley, T., 1903, 83, 43; P., 1904, 20, 92). The same compound, m. p. 191° , is also produced by the action of a small quantity of nitric acid (*d* 1.46) on a solution of *isonitrosomalondimethylanilide* in chloroform saturated with nitrosyl chloride, but under these conditions the secondary products are *nitromalondimethylanilide*, $(\text{NMePh}\cdot\text{CO})_2\text{CH}\cdot\text{NO}_2$, and *chloromalondimethylanilide*, $(\text{NMePh}\cdot\text{CO})_2\text{CHCl}$. When nitric acid alone acts on a solution of the *isonitroso*-compound in chloroform, a very small quantity of the compound, m. p. 191° , is formed, the chief product of the reaction being the nitro-compound. Finally, the compound, m. p. 191° , can be prepared conveniently by the direct oxidation of the *isonitroso*-compound with chromic acid in hot glacial acetic acid solution.

The reactions of the compound $\text{C}_{17}\text{H}_{15}\text{O}_3\text{N}_3$, m. p. 191° , show that it contains only one carboxylmethylanilide group ($-\text{CO}\cdot\text{NMePh}$) and does not contain the *isonitroso*-group, hence it must be assumed that the two atoms of hydrogen eliminated by oxidation from *isonitrosomalondimethylanilide* have been provided by the *isonitroso*-group and either the methyl or phenyl group of one of the carboxylmethylanilide groups, and the compound, m. p. 191° , contains the five-membered glyoxaline ring, as in Ia, or the six-membered quinoxaline ring, as in I.



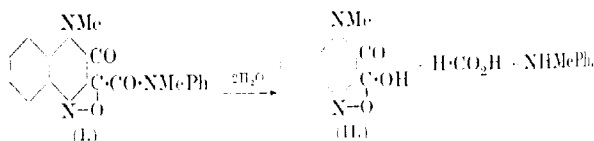
according as the second hydrogen atom is eliminated from the methyl group or from the ortho-position of the phenyl group.

The work described in the present communication shows conclusively that the compound $\text{C}_{17}\text{H}_{15}\text{O}_3\text{N}_3$, m. p. 191° , is a derivative of tetrahydroquinoxaline and has the structure represented by (I). This result has been achieved by breaking down the compound into simpler products which are known already, or can be prepared by rational syntheses.

Oxidation reactions, which are often of great value in determining the structure of organic compounds, throw little light on the present problem. The compound is very stable towards oxidising agents, and can, in fact, be prepared by the action of chromic acid on a boiling acetic acid solution of isonitrosomalondimethylanilide. It is more easily attacked by alkaline permanganate, but the only product that has been isolated is methylphenyloxamic acid, which serves to prove the presence in the molecule of the group $>\text{C} \cdot \text{CO} \cdot \text{NMePh}$.

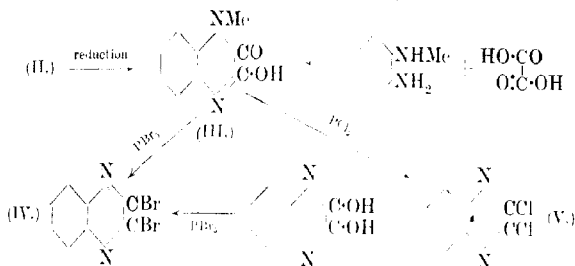
Other methods of attack, however, have proved more useful in giving derivatives which preserve the ring structure present in the parent compound.

When the compound (I), m. p. 191° , is treated with an alcoholic solution of sodium ethoxide, hydrolysis occurs, and a sodium salt is precipitated from which a strong acid (II), m. p. 256° , can be obtained by the action of mineral acids. The other products of the reaction, methylaniline and formic acid, can be isolated from the alcoholic mother-liquor in the form of *p*-toluenesulphonmethylanilide and lead formate, respectively.



The action on (II) of oxidising agents or of stronger hydrolysing agents does not lead to the formation of any easily recognisable derivatives. On the other hand, reducing agents convert (II) into a simpler compound (III), m. p. $281-283^\circ$, the structure of which as *2-keto-3-hydroxy-1-methyl-1:2-dihydroquinoxaline* has been established in three ways: (1) By its synthetic formation from

N-methyl-*o*-phenylenediamine and oxalic acid. (2) On treatment with phosphorus pentabromide, the compound (III) gives a dibromo-derivative (IV) which has been proved to be 2:3-dibromo-quinoxaline by the synthesis of this compound from 2:3-dihydroxy-quinoxaline and phosphorus pentabromide. (3) By the action of phosphorus pentachloride the compound (III) is converted into the known compound 2:3-dichloroquinoxaline (V):

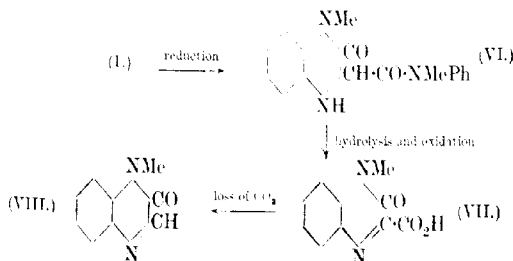


The removal of the alkyl group by the action of the phosphorus pentahalides in the last two reactions appears to be general among the nitrogen-substituted quinoxalines, for Hinsberg (*Annalen*, 1896, **292**, 257) has shown that 3-keto-2-hydroxy-4-benzyl-1:2-dihydroquinoxaline yields 2:3-dichloroquinoxaline and benzyl chloride on treatment with phosphorus pentachloride:



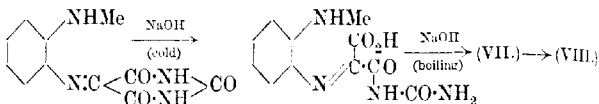
Another process by which the compound (I) has been broken down into a known quinoxaline derivative is as follows:

The compound (I) is readily reduced to the compound (VI), which on treatment with sodium ethoxide suffers simultaneous

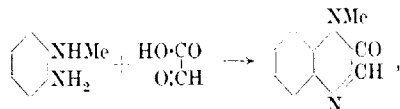


hydrolysis and oxidation, yielding the sodium salt of the carboxylic acid (VII). This acid on heating readily loses carbon dioxide and is converted into the basic substance (VIII).

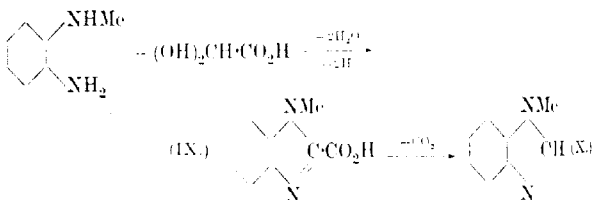
The acid (VII) (2-keto-1-methyl-1:2-dihydroquinoxaline-3-carboxylic acid) and the base (VIII) (2-keto-1-methyl-1:2-dihydroquinoxaline) are known compounds, having been prepared by Kühling and Kaselitz (*Ber.*, 1906, **39**, 1325) from alloxanmethyl-*o*-phenylenediamine.



An attempt was made to synthesise the base (VIII) by a more direct method than that employed by Kühling and Kaselitz. It was expected that *N*-methyl-*o*-phenylenediamine would condense with glyoxylic acid in accordance with the scheme

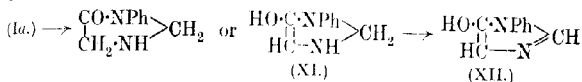


producing the base (VIII). Experiment showed, however, that this condensation gives rise exclusively to the compound (IX), and this readily loses carbon dioxide, giving the base (X), *N*-methylbenzimidazole, which has been described by Fischer and Wreszinski (*Ber.*, 1892, **25**, 2711).



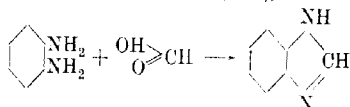
The course taken in the preceding condensation is only one of the many illustrations that might be given to show the remarkable tendency to formation of the glyoxaline ring, and, in the earlier stages of this work, it was thought possible that one of the hydrogen atoms removed by oxidation from the molecule of the *is*-nitrosomalondimethylanilide might be one of the hydrogens of a *N*-methyl group. This would lead to the glyoxaline structure (Ia) for the compound now known to have the structure (I), and with this possibility in view a series of experiments was made with the object of synthesising a compound having the structure (Ia), or

compounds containing a similar ring into which it was expected that this compound might be degraded by the use of suitable reagents. One of the simplest compounds into which a substance having the structure Ia could be converted without loss of the five-membered ring nucleus is the compound (XI); but in view of the extraordinary stability of the glyoxaline nucleus towards reducing agents a compound such as (XI) would probably lose hydrogen to give the simpler compound (XII).

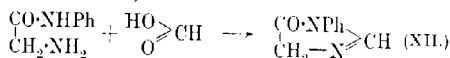


Attempts to synthesise a compound having the structure represented by XII fall into three main divisions:

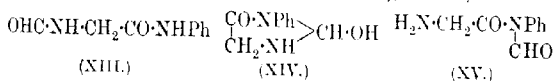
1. Since *o*-phenylenediamine and formic acid condense to give benziminazole (Wundt, *Ber.*, 1878, **11**, 826),



it was not unreasonable to suppose that a compound having the structure (XII) would be produced in the condensation of glycine-anilide with formic acid,



When, however, formic acid acts on glycineanilide, it yields a formyl derivative having the structure (XIII), (XIV), or (XV).

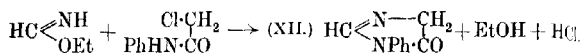


All attempts to induce further condensation by the removal of the elements of water from the formyl compound have been unsuccessful. Most dehydrating agents appear to break down the molecule, as aniline is usually found among the products of such reactions. Acetic anhydride, however, gives rise to a mono-acetyl derivative.

2. Finger (*J. pr. Chem.*, 1907, [ii], **76**, 93) has shown that acetoimidoethyl ether and glycine ester condense to form a glyoxaline ring:

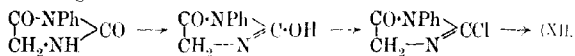


It was hoped that formimidoethyl ether and chloroacetanilide might condense in a somewhat similar manner to give the glyoxaline derivative (XII):



Experiment showed, however, that no condensation occurred between these compounds.

3. The close structural resemblance between phenylhydantoin and the glyoxaline compound (XII) suggested that the former compound might be converted into the latter by means of the following series of reactions:



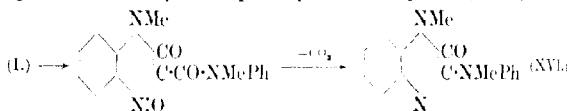
The experiment was unsuccessful, as the required chloro-derivative could not be prepared.

Action of Concentrated Sulphuric Acid on the Quinoxaline Compound

(I) (3:4-Oxido-2-keto-1-methyl-1:2:3:4-tetrahydroquinoxaline-3-carboxymethylanilide).

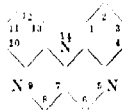
The quinoxaline compound (I) is very readily attacked by concentrated sulphuric acid and yields one or both of two products according to the conditions of the experiment.

1. When the quinoxaline compound is added gradually to cold concentrated sulphuric acid, it develops a bright red colour and dissolves with loss of carbon dioxide to form the tertiary basic substance (XVI) 3-phenylmethylamino-2-keto-1-methyl-1:2-dihydroquinoxaline together with a very small quantity of the compound (XVII).



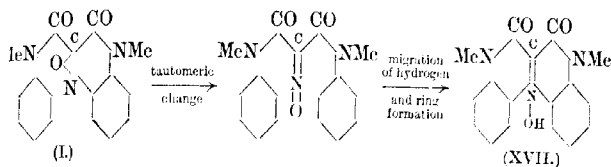
2. If, on the other hand, concentrated sulphuric acid be dropped on to the quinoxaline compound, there is an immediate and violent reaction, accompanied by the evolution of a small quantity of carbon dioxide, and development of a bright red colour—a small quantity of the basic substance (XVI) is formed, but the chief product of the reaction is insoluble in dilute acids, and has been identified as the sulphonic derivative of the heterocyclic ring compound (XVII)*, due to the formation of a second quinoxaline com-

* The compound (XVII) appears to be the first instance of the ring



and it is suggested that the empirical name *malonaniline* be given to it; the name indicating that the ring is derived from malonanilide.

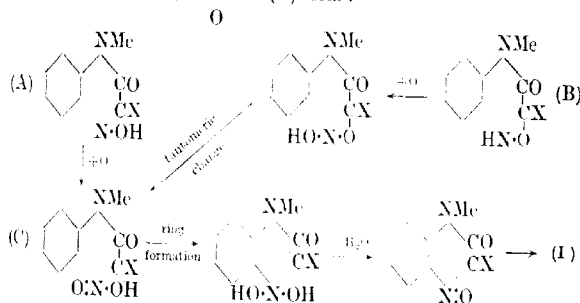
plex by migration of hydrogen from the ortho-position of the remaining phenyl group to the oxygen of the oxido-ring in (I), acting in its tautomeric form.



Mechanism of the Formation of the Quinoxaline Compound (I) from isoNitrosomalondimethylanilide by Oxidation.

It has been shown conclusively that the quinoxaline compound, m. p. 191° , is derived from *isonitrosomalondimethylanilide* by the removal by oxidation of two atoms of hydrogen, one from the *isonitroso*-group and one from the *ortho*-position of one of the phenyl groups of this compound. The mechanism of this change merits special consideration, since it is improbable that the reaction consists in the direct removal of the two hydrogen atoms by an oxygen atom. Probably the first stage in the reaction consists in the addition of an atom of oxygen to the nitrogen of the *isonitroso*-group; the hydrogen atom in the *ortho*-position of the neighbouring phenyl group then passes over to this oxygen atom, forming a ring compound, which on loss of the elements of water is converted into the quinoxaline compound (I).

This series of changes can be expressed in two ways according as to whether the *isonitroso*-group is written in the oxime $>\text{C}:\text{NOH}$ (A) or the *isooxime* $>\text{C}=\text{N}\cdot\text{OH}$ (B) form :

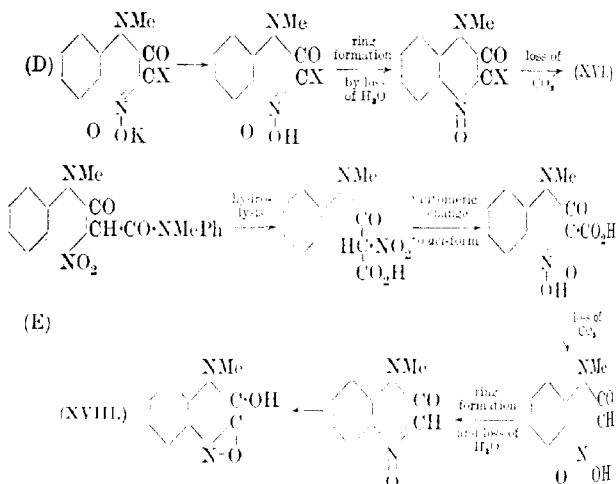


Now, whichever of these schemes is the true representation of the complete course of the reaction, each requires the intermediate

formation of the *aci*-form of nitromalondimethylanilide, from which the quinoxaline compound is derived by the loss of a molecule of water between the hydrogen atom in the ortho-position of a phenyl group, and the hydroxyl group of this active form of the nitro-compound, and the following experiments show that if the nitro-compound be liberated from its salts in the presence of a reagent which can induce condensation with ring formation, the quinoxaline compound, m. p. 191°, or one of its direct derivatives, will be produced:

1. When the nitro-compound is liberated from its salts in the presence of a mixture of nitric and nitrous acids, then the quinoxaline compound (I) and some regenerated nitro-compound are the sole product of the reaction, the course of which is shown above (C).

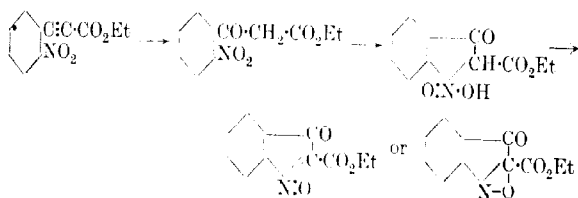
2. When nitromalondimethylanilide, or its alkali salt, is treated with concentrated sulphuric acid, a very small quantity of the base (XVI) is produced, indicating that to a limited extent the nitro-compound reacts in its *aci*-form as shown in (D) below; the chief product of the reaction, however, is the simpler quinoxaline compound (XVIII), 3:4-*oxido-2-hydroxy-1-methyl-1:4-dihydroquinoxaline*, similarly produced from the partly hydrolysed nitro-compound as shown in (E) below:



Although the suggestion that the quinoxaline compound (I) is derived from the *aci*-form of nitromalondimethylanilide receives

support from the experimental evidence cited above, this explanation of the mechanism of the reaction is not wholly satisfactory, for it fails to account for the formation of the quinoxaline compound together with mesoxdimethylanilide by the action of nitrosyl chloride and water on isonitrosomalondimethylanilide. Moreover, nitromalondimethylanilide itself yields (1) *chloronitromalondimethylanilide* when treated with nitrosyl chloride and nitric acid, and (2) mesoxdimethylanilide when oxidised with chromic acid; and, further, nitromalondimethylanilide yields no quinoxaline derivative when treated with such dehydrating agents as acetic anhydride or phosphoryl chloride.

The explanation of the mechanism of ring formation by internal condensation suggested in (A), (B), (C), (D), and (E) above is probably of general application. Thus the hitherto unexplained formation of isotogenic ester from *o*-nitrophenylpropionic ester (Baeyer, *Ber.*, 1881, 14, 1741) in all probability depends on this type of change; for it may be assumed that, in the presence of concentrated sulphuric acid, the *o*-nitrophenylpropionic ester is first transformed into *o*-nitrobenzoylacetate ester. The hydrogen atom from the methylene group in this compound then migrates to the oxygen of the nitro-group, and subsequent loss of water leads to the formation of isotogenic ester:



A similar explanation can also be offered of the conversion of di(*o*-nitrophenyl)-diacetylene into di-isatogen (Baeyer, *Ber.*, 1882, 15, 53), and of *o*-nitrobenzylmalonic acid into *N*-hydroxyindole-carboxylic acid (Reisert, *Ber.*, 1896, 29, 646) in the presence of alkali.

EXPERIMENTAL.

I. Preparation of 3:4-Oxido-2-keto-1-methyl-1:2:3:4-tetrahydro-quinoxaline-3-carboxymethylanilide (I) from isonitrosomalondimethylanilide.

The quinoxaline compound (I) has been prepared from isonitrosomalondimethylanilide by four different reactions:

1. *By the action of nitrosyl chloride and nitric acid.*—In this reaction it is not necessary to isolate the isonitroso-compound,

therefore 5 grams of malondimethylanilide, dissolved in 20 c.c. of chloroform cooled at -5° , were converted into the isonitroso-compound by saturating the solution with nitrosyl chloride. After keeping it at the low temperature during thirty minutes, the solution was treated with 0.5 c.c. of a mixture of equal volumes of concentrated and fuming nitric acids; there was a vigorous reaction and the temperature rose to about 40° . When a drop of the solution on evaporation left a residue that gave no purple coloration with alkali and ferrous sulphate (reaction characteristic of the isonitroso-compound), the solution was allowed to evaporate rapidly and spontaneously. The residual syrup became crystalline on treatment with a small quantity of alcohol, the crystals consisting of a mixture of *nitro-* and *chloro-malondimethylanilide* together with the quinoxaline compound (I), from which mixture the nitro-compound was removed by repeated extraction with hot solution of sodium carbonate; owing to the similar solubility in all solvents of the remaining constituents of the mixture, they could not be separated by fractional crystallisation, but as the chloro-compound crystallises from ethyl alcohol in large, and the quinoxaline compound in thin, flattened, prisms, these compounds were separated originally by mechanical methods. Subsequently it was found more convenient to remove the chloromalondimethylanilide by reduction to malondimethylanilide under conditions that do not affect the quinoxaline compound (I) (West, T., 1922, **121**, 2198). Twenty grams of the crystalline mixture dissolved in glacial acetic acid were warmed during half an hour with excess of potassium iodide. The solution was poured into water, and after the originally oily precipitate had solidified, the excess of iodine was removed by means of sulphur dioxide. The crystalline product after crystallising from alcohol consisted of the pure *quinoxaline* compound (I).

From 50 grams of malondimethylanilide, treated as described above in batches of 5 grams each, 20 grams of the nitro-compound, 7 grams of the chloro-compound, and 16 grams of the quinoxaline compound were obtained: but the total yield, as well as the relative proportions of each constituent, varied greatly with the conditions of the experiment.

3:4-Oxido-2-keto-1-methyl-1:2:3:4-tetrahydroquinoxaline-3-carboxylmethylanilide is readily soluble in each of the ordinary organic solvents with the exception of ether, carbon tetrachloride, and petroleum. It crystallises from ethyl or methyl alcohol in pale yellow, thin, flattened prisms that melt at $190-191^{\circ}$, and have a bitter taste [Found: C = 65.8; H = 4.9; N = 13.7; *M* (in naphthalene) = 312. $C_{17}H_{15}O_3N_3$ requires C = 66.0; H = 4.8; N = 13.6 per cent.; *M* = 309]. This compound dissolves in concentrated

sulphuric acid, yielding a characteristic bright red solution containing the compounds (XVI) and (XVII). It is converted into the compound (VI) on reduction; and yields compound (II) on hydrolysis. These reactions are described fully under their respective headings.

Whilst the quinoxaline compound (I) is not attacked by acetic anhydride, benzoyl chloride, or benzenesulphonyl chloride, acetyl chloride converts it into an *acetyl* derivative, containing chlorine, which crystallises from slightly diluted acetic acid in colourless, hexagonal prisms melting at 226° (Found: C = 61.5; H = 4.5; Cl = 9.2; N = 11.3. $C_{19}H_{18}O_3N_3Cl$ requires C = 61.4; H = 4.8; Cl = 9.6; N = 11.3 per cent.); and, further, hydrogen chloride or concentrated hydrochloric acid acts on an alcoholic solution of the quinoxaline compound (I) to form a *chloro*-compound that crystallises from alcohol in colourless, rectangular prisms melting at $240-241^{\circ}$ (Found: C = 61.8; H = 5.0; N = 12.9; Cl = 10.7. $C_{17}H_{16}O_2N_3Cl$ requires C = 61.9; H = 4.9; N = 12.8; Cl = 10.8 per cent.). Each of these chloro-compounds is stable towards reducing agents, and yields methylaniline on hydrolysis, but the other products of hydrolysis have not been identified, and no satisfactory structural formula can be assigned to these compounds at present.

Nitromalondimethylanilide, $(CO \cdot NMePh)_2CH \cdot NO_2$, is readily soluble in all the ordinary organic solvents with the exception of ether, carbon tetrachloride, and petroleum, in which it is insoluble. It crystallises in large, well-formed, colourless prisms, that melt at 156° , and are tasteless. On reduction with zinc and acetic acid, it yields mesoxdimethylanilide (Found: N = 12.91. $C_{17}H_{17}O_4N_3$ requires N = 12.84 per cent.). Nitromalondimethylanilide dissolves readily in caustic alkali solutions, less readily in sodium carbonate solution; the solutions are yellow, but yield the original colourless nitro-compound on treatment with mineral or acetic acid. The *potassium* salt is precipitated in a crystalline form when a warm solution of 1.5 grams (1.5 mols.) of potassium hydroxide in 20 c.c. of alcohol is added to a hot solution of 5 grams (1 mol.) of the nitro-compound in 50 c.c. of alcohol: after recrystallising from alcohol, the salt forms pale yellow, thin prisms that have a bitter taste (Found: K = 10.33. $C_{17}H_{16}O_4N_3K$ requires K = 10.64 per cent.).

Chloronitromalondimethylanilide, $(CO \cdot NMePh)_2Cl \cdot NO_2$, is obtained in small quantity when nitric acid acts on a solution of nitromalondimethylanilide in chloroform, saturated with nitrosyl chloride. From 1 gram of the nitro-compound dissolved in 40 c.c. of chloroform, saturated with nitrosyl chloride at -5° and then

treated with 2 c.c. of nitric acid (d 1.46), 0.9 gram of the *chloronitro*-compound was obtained. It crystallises from alcohol in colourless leaflets melting at $132\text{--}134^\circ$ (Found: C = 56.7; H = 4.6; Cl = 9.4. $\text{C}_{17}\text{H}_{16}\text{O}_4\text{N}_3\text{Cl}$ requires C = 56.4; H = 4.4; Cl = 9.8 per cent.).

Chloromalondimethylanilide, $(\text{CO}\cdot\text{NMePh})_2\text{CHCl}$, is a by-product in the preparation of *isonitrosomalondimethylanilide* by the action of nitrosyl chloride on malondimethylanilide. It dissolves readily in methyl alcohol or acetic acid, is less readily soluble in all the other organic solvents with the exception of ether and carbon tetrachloride, in which it is insoluble; it forms colourless, well-developed prisms that melt at 185° . It is readily reduced by the action of zinc and acetic acid or by hydriodic acid, to malondimethylanilide (Found: C = 64.09; H = 5.57; N = 8.94; Cl = 11.28. $\text{C}_{17}\text{H}_{17}\text{O}_2\text{N}_2\text{Cl}$ requires C = 64.46; H = 5.38; N = 8.85; Cl = 11.20 per cent.).

2. *By the action of water on a solution of isonitrosomalondimethylanilide in chloroform saturated with nitrosyl chloride.*—A solution of 5 grams of malondimethylanilide in 30 c.c. of chloroform was saturated with nitrosyl chloride at 0° , and after about thirty minutes it was treated with a few drops of water and the mixture shaken, when there was a vigorous evolution of nitrous fumes and of hydrogen chloride and heat was developed. After a few minutes, when the solution no longer contained any of the *isonitroso*-compound, the chloroform and excess of nitrosyl chloride were removed by rapid and spontaneous evaporation. The crystalline residue, after being washed with a little cold methyl alcohol, was found to be a mixture of the quinoxaline compound (I) with the ketonic compound, *mesoxdimethylanilide*, and weighed 3.1 grams. Separation was effected by adding one part of cold water to two parts of a hot alcoholic solution of the mixture, when the ketonic compound crystallised on cooling, and the quinoxaline compound was recovered from the mother-liquor.

Mesoxdimethylanilide, $(\text{CO}\cdot\text{NMePh})_2\text{CO}$, is very readily soluble in methyl alcohol, acetic acid, chloroform, benzene, or pyridine, fairly soluble in ethyl alcohol, ethyl acetate, carbon tetrachloride, or toluene, sparingly soluble in ether, and insoluble in petroleum; it crystallises in long, thin, pale yellow prisms, melting at 171° , and is tasteless. It yields *isonitrosomalondimethylanilide* on treatment with hydroxylamine in slightly alkaline solution (Found: C = 68.18; H = 5.48; N = 9.55. $\text{C}_{17}\text{H}_{16}\text{O}_3\text{N}_2$ requires C = 68.92; H = 5.46; N = 9.46 per cent.).

When preparing *mesoxdimethylanilide* by the method described above, it was found, not infrequently, to be mixed with a small quantity of a *secondary product* which is soluble in sodium carbonate

solution. At present the constitution of this compound is undetermined; it crystallises in pale yellow, thin, flattened prisms from alcohol and melts at 170° (Found: C = 59.97; H = 4.86; N = 16.47. $C_{17}H_{16}O_4N_4$ requires C = 59.99; H = 4.71; N = 16.47 per cent.).

Mesoxdimethylanilide has been prepared also by the action of the nitrogen oxides evolved from arsenious oxide and nitric acid (*d* 1.3) on isonitrosomalondimethylanilide, dissolved in moist chloroform, alcohol, or acetic acid; moreover, it is the only product that has been isolated when nitromalondimethylanilide is reduced by means of zinc and acetic acid (5 grams of the nitro-compound yielded 2–3 grams of the ketone); and, finally, nitromalondimethylanilide yields a very small quantity of mesoxdimethylanilide when oxidised by chromic acid in acetic acid solution (5 grams of the nitro-compound gave less than 0.1 gram of the ketone). It is hoped that further work will throw some light on the mechanism of these reactions.

3. *By the action of chromic acid.*—Five grams of isonitrosomalondimethylanilide, dissolved in 30 c.c. of glacial acetic acid, were boiled for fifteen minutes with 14 c.c. (= two atoms of oxygen) of a solution of chromium trioxide in acetic acid (50 grams of CrO_3 in 350 c.c.). The product was poured into water, excess of chromic acid reduced by means of sulphur dioxide, the solution filtered from a small amount of a brown, amorphous solid, and the filtrate extracted with chloroform. The chloroform extract left a syrupy residue on evaporation which yielded 1.7 grams of crystalline matter on treatment with alcohol, and was found to be the quinoxaline compound (I). After crystallisation from alcohol, it melted at 189 – 191° and did not depress the melting point of an authentic specimen of this compound.

4. *By the action of nitric acid.*—Five grams of isonitrosomalondimethylanilide, dissolved in 30 c.c. of chloroform, were treated with 2 c.c. of a mixture of equal volumes of concentrated and fuming nitric acids, and the mixture warmed until the solvent began to boil. The solution was then allowed to evaporate spontaneously and the residual syrup treated with alcohol: this gave 2.9 grams of crystalline material which was found to be a mixture of nitromalondimethylanilide (2.3 grams), m. p. 156° , with the quinoxaline compound (I) (0.3 gram), m. p. 189 – 191° .

Oxidation of 3:4-Oxido-2-keto-1-methyl-1:2:3:4-tetrahydro-3-carboxylmethylanilide (I) with Potassium Permanganate.

To 5 grams of the quinoxaline compound (I), suspended in 100 c.c. of hot 2*N*-sodium carbonate solution containing magnesium

sulphate, a quantity of 4 per cent. potassium permanganate solution (equivalent to 12 atoms of oxygen) was added slowly. After removing the manganese, the solution was reduced in bulk, and 1.1 grams of the unchanged compound were separated by filtration and ether extraction. From the acidified solution ether extracted 0.6 gram of methylphenyloxamic acid, which crystallised from water in colourless prisms melting at 82° , or at 129° (decomp.) after drying; the anhydrous acid, m. p. 130° , was also obtained by crystallising from benzene. Guareschi (private communication to Beilstein) gives m. p. 82° (hydrated) or 120° (decomp.) (anhydrous). The acid yields methylaniline on decomposition at its melting point (Found: C = 60.7; H = 5.1. Calc., C = 60.3; H = 5.0 per cent.).

Degradation of 3:4-Oxido-2-keto-1-methyl-1:2:3:4-tetrahydroquinoxaline-3-carboxylmethylanilide (I) to 2-Keto-3-hydroxy-1-methyl-1:2-dihydroquinoxaline (III).

1. *3:4-Oxido-2-keto-3-hydroxy-1-methyl-1:2:3:4-tetrahydroquinoxaline (II).*—To 5 grams of the quinoxaline compound (I), suspended in 25 c.c. of alcohol, 30 c.c. of a solution of sodium ethoxide (5 per cent.) were added and the mixture was warmed on the water-bath until solution was complete. A gelatinous sodium salt was precipitated which redissolved on the addition of a little water and then separated in colourless prisms (Found: Na = 10.24. $C_9H_7O_3N_2Na$ requires Na = 10.7 per cent.). The potassium salt, prepared similarly from the quinoxaline compound and alcoholic potassium hydroxide, crystallises in plates (Found: K = 17.19. $C_9H_7O_3N_2K$ requires K = 16.99 per cent.). The acidic compound (II), *3:4-oxido-2-keto-3-hydroxy-1-methyl-1:2:3:4-tetrahydroquinoxaline*, is precipitated by mineral acids from aqueous solutions of the alkali salts. It is readily soluble in methyl alcohol, acetic acid, or hot water, sparingly soluble in ethyl alcohol, ethyl acetate, or ether, and insoluble in the other ordinary solvents: it crystallises from alcohol in stellate clusters of colourless, brilliant, long prisms that melt at 257° (decomp.) (Found: C = 56.4; H = 4.4; N = 14.59. $C_9H_8O_3N_2$ requires C = 56.25; H = 4.17; N = 14.58 per cent.). This compound has a bitter taste, dissolves readily in alkali carbonates, and gives an *ethyl ether* that melts at 167 – 168° [Found: C = 60.5; H = 5.83; N = 12.8; *M* (in naphthalene) = 221. $C_{11}H_{12}O_3N_2$ requires C = 60.0; H = 5.45; N = 12.73 per cent.; *M* = 220].

2. *2-Keto-3-hydroxy-1-methyl-1:2-dihydroquinoxaline (III).*—Four grams of the compound (II), reduced by zinc dust (2 grams) in boiling acetic acid solution, yielded 2.8 grams of a product that

melted at 281–283° after crystallising from hot water, from which it separates in thin prisms forming a loose lattice-like structure; it can also be crystallised from acetic acid, but is very sparingly soluble in all the other organic solvents (Found: C = 61.4; H = 4.7. $C_8H_8O_2N_2$ requires C = 61.4; H = 4.5 per cent.). This compound has been identified as 2-keto-3-hydroxy-1-methyl-1:2-dihydroquinoxaline by converting it into (i) 2:3-dichloroquinoxaline, (ii) 2:3-dibromoquinoxaline, and (iii) by comparison with a synthetic specimen.

(i) *Conversion into 2:3-Dichloroquinoxaline*.—One gram of the compound (III) was heated with 2.4 grams of phosphorus pentachloride at 160° until there was no further reaction. The product was poured into water, and the solid that separated after twice crystallising from alcohol was obtained as nearly colourless, brilliant scales melting at 148–150°. It was identified as 2:3-dichloroquinoxaline by direct comparison, and by the melting-point test, with a synthetic specimen prepared from 2:3-dihydroxyquinoxaline by Hinsberg and Pollak's method (*Ber.*, 1895, 29, 784).

(ii) *Conversion into 2:3-Dibromoquinoxaline*.—One gram of the compound (III) was heated at 140° with 5.5 grams of phosphorus pentabromide until the reaction ceased. On pouring into water, a solid separated that crystallised from alcohol in colourless, thin leaflets melting at 171–174° (Found: C = 33.1; H = 1.7; N = 10.0; Br = 55.4. $C_8H_4N_2Br_2$ requires C = 33.3; H = 1.4; N = 9.7; Br = 55.6 per cent.).

This compound was found to be identical with a synthetic specimen of 2:3-dibromoquinoxaline, prepared by heating 1 gram of 2:3-dihydroxyquinoxaline (prepared by Hinsberg and Pollak's method, *loc. cit.*) with 5.5 grams of phosphorus pentabromide at 140–160°. The product, after crystallising from alcohol, melted at 170–172° and did not depress the melting point of the compound prepared from (III) above.

(iii) *Synthesis of 2-Keto-3-hydroxy-1-methyl-1:2-dihydroquinoxaline (III)*.—A mixture of *N*-methyl-*o*-phenylenediamine (1.6 grams) (prepared as described on p. 1084) with anhydrous oxalic acid (1.8 grams) was heated at 140–160° until there was no further evolution of steam. After removing the excess of oxalic acid with warm water, the residue was crystallised first from acetic acid, then from water; it crystallised from the latter solvent in the colourless, thin needles, forming the loose lattice structure characteristic of compound (III), and melted at 281–283°.

Degradation of 3:4-Oxido-2-keto-1-methyl-1:2:3:4-tetrahydroquinoxaline-3-carboxymethylanilide (I) to 2-Keto-1-methyl-1:2-dihydroquinoxaline-3-carboxylic Acid (VII), and to 2-Keto-1-methyl-1:2-dihydroquinoxaline (VIII).

1. *2-Keto-1-methyl-1:2:3:4-tetrahydroquinoxaline-3-carboxymethylanilide (VI).*—Five grams of the quinoxaline compound (I), dissolved in 100 c.c. of glacial acetic acid, were reduced at 0° by adding gradually 5 grams of zinc dust while the mixture was shaken. After filtering, the reduced compound (VI) was obtained in a crystalline form (4.5 grams) by adding water to the filtrate. It crystallises from alcohol in well-formed, thin prisms melting at 185°, which are tasteless (Found: C = 69.02; H = 5.86; N = 14.9. $C_{17}H_{11}O_2N_3$ requires C = 69.15; H = 5.76; N = 14.23 per cent.).

2. *2-Keto-1-methyl-1:2-dihydroquinoxaline-3-carboxylic Acid (VII) and 2-Keto-1-methyl-1:2-dihydroquinoxaline (VIII).*—The compound (VI) (3 grams), suspended in 15 c.c. of alcohol, was heated on the steam-bath with 25 c.c. of sodium ethoxide solution (5 per cent.). The solid passed into solution and when hydrolysis was complete the sodium salt of 2-keto-1-methyl-1:2-dihydroquinoxaline-3-carboxylic acid was precipitated in a gelatinous form, from which the acid was liberated by mineral acid. This acid (1.3 grams) crystallises from acetic acid in pale yellow leaflets, m. p. 173–174° (decomp.). Kühling and Kaselitz (*loc. cit.*) give m. p. 174° (decomp.) (Found: C = 59.2; H = 4.0. Calc., C = 58.8; H = 3.9 per cent.).

The carboxylic acid (VII) decomposes at its melting point, losing carbon dioxide and giving the compound (VIII), 2-keto-1-methyl-1:2-dihydroquinoxaline, which can be purified by sublimation. It is sparingly soluble in water, from which it crystallises in colourless needles, and dissolves readily in all the ordinary organic solvents with the exception of light petroleum, and it melts at 122° (Kühling and Kaselitz give m. p. 122°) (Found: C = 67.2; H = 5.2; N = 17.5. Calc., C = 67.5; H = 5.0; N = 17.5 per cent.).

Condensation of N-Methyl-o-phenylenediamine with Glyoxylic Acid. Formation of 1-Methylbenzimidazole-2-carboxylic Acid (IX).

1. *Preparation of N-Methyl-o-phenylenediamine.*—This compound was prepared from o-nitroaniline by methylation and subsequent reduction.

A solution of pure o-nitroaniline (55.5 grams) and p-toluenesulphonyl chloride (76.6 grams) in pyridine was heated on the steam-bath during four hours. On pouring the solution into water,

the *p*-toluenesulphon-*o*-nitroanilide separated as an oil that solidified on rubbing. The crude product weighed 99.5 grams and yielded 87.5 grams of the pure compound, m. p. 112—114°, after crystallising from alcohol.

The *p*-toluenesulphon-*o*-nitroanilide was methylated by suspending portions of 8 grams in 40 c.c. of sodium hydroxide solution (10 per cent.) and adding 30 c.c. of methyl sulphate in successive portions of 5 c.c., with continual shaking, further quantities of sodium hydroxide solution being added as necessary (about 60 c.c.) to keep the liquid alkaline. The precipitate of *p*-toluenesulphon-methyl-*o*-nitroanilide (8.6 grams) crystallised from alcohol in colourless prisms melting at 130—132°.

The methylated product (63 grams) was hydrolysed by heating for one hour on the steam-bath with a mixture of 31.5 c.c. of glacial acetic acid and 71 c.c. of concentrated sulphuric acid. On pouring the product into water, *o*-nitromethylaniline separated as an oil which gradually solidified to an orange, crystalline solid (19.8 grams) that melted at 34—35° (Hempel, *J. pr. Chem.*, 1890, [ii], **41**, 164, gives m. p. 26—28°; Kehrman and Messenger, *ibid.*, 1892, [ii], **46**, 365, give m. p. 34°).

The *o*-nitromethylaniline (32 grams) on reduction with tin and hydrochloric acid gave 21.9 grams of *N*-methyl-*o*-phenylenediamine boiling at 245—251° and yielding a hydrochloride melting at 192—193° (decomp.) [Fischer, *Ber.*, 1892, **25**, 2841, gives m. p. 191° (decomp.)].

2. *Condensation of Glyoxylic Acid with N-Methyl-o-phenylenediamine. Formation of 1-Methylbenzimidazole-2-carboxylic Acid (IX).*—Preliminary experiment showed that on mixing glyoxylic acid with *N*-methyl-*o*-phenylenediamine, either alone or dissolved in ether, alcohol, acetic acid, or dilute hydrochloric acid, a violent reaction takes place with elimination of carbon dioxide and development of heat. Under the following conditions, however, the condensation can be effected without the loss of carbon dioxide.

Glyoxylic acid (0.94 gram), dissolved in a small quantity of water and cooled in ice, was added drop by drop to a solution of 1.23 grams of *N*-methyl-*o*-phenylenediamine in dilute acetic acid cooled at -14°. The temperature of the mixture was allowed to rise gradually to about 5°, and the solid product of the reaction (0.4 gram) separated by filtration. This compound (IX) dissolves with effervescence in sodium hydrogen carbonate, and is reprecipitated by mineral acids from concentrated solutions. It is readily soluble in water, methyl or ethyl alcohol, acetic acid, or ethyl acetate, and insoluble in the other ordinary organic solvents. The compound, purified for analysis by crystallising from water below 60°, forms

long, colourless, flattened prisms, m. p. 98—99° (decomp.) (Found: C = 61.4; H = 4.7; N = 15.9. $C_9H_8O_2N_2$ requires C = 61.4; H = 4.5; N = 15.9 per cent.). This acid, 1-methylbenzimidazole-2-carboxylic acid, lost carbon dioxide at its melting point, forming a colourless oil that solidified to crystals melting at about 30°; owing to lack of material it was not possible to obtain a pure specimen of this compound, N-methylbenzimidazole (X); according to Fischer and Wreszinski (*Ber.*, 1892, **25**, 2711), it melts at 33°.

Condensation of Glycineanilide with Formic Acid.

Attempts to prepare glycineanilide from ammonia and chloroacetanilide, or from aniline and glycine ester were unsuccessful (compare Majert, D.R.-P. 59121, 59874). Ultimately it was found possible to prepare *glycineanilide carbonate* by the action of the hydrochloride of glycine chloride (1 mol.) (Fischer, *Ber.*, 1905, **38**, 2917) on aniline (2 mols.), dissolved in dry chloroform, and treating with sodium carbonate solution the residue left on evaporation of the chloroform. *Glycineanilide carbonate* was purified by solution in dilute hydrochloric acid and reprecipitation with pure sodium carbonate solution, the precipitate being washed with water, alcohol, and ether successively (Found: C = 56.8; H = 6.1. $C_{11}H_{12}O_3N_2$ requires C = 56.4; H = 6.1 per cent.). This salt is not stable, and loses carbon dioxide on keeping.

Condensation of Glycineanilide Carbonate with Formic Acid.—Glycineanilide carbonate (4.2 grams) and 2.8 c.c. of formic acid (98 per cent.) were heated on the steam-bath for two hours, and the crystals that separated on cooling were drained on porous earthenware and crystallised from water. The product, 2-hydroxy-4-*ke*-to-3-phenyltetrahydroglyoxaline (XIV) or formyluminoacetanilide (XIII), crystallises in short, thin needles, m. p. 148—150° (Found: C = 60.3; H = 5.8. $C_9H_{10}O_2N_2$ requires C = 60.7; H = 5.6 per cent.). It yields an *acetyl* derivative that crystallises from a mixture of benzene and alcohol in minute, colourless needles, m. p. 168—171° (Found: C = 59.7; H = 5.6. $C_{11}H_{12}O_3N_2$ requires C = 60.0; H = 5.5 per cent.).

Behaviour of 3:4-Oxido-2-ke-to-1-methyl-1:2:3:4-tetrahydroquinoxaline-3-carboxylmethylanilide (I) towards Concentrated Sulphuric Acid.

1. *Preparation of 3-Phenylmethylumino-2-ke-to-1-methyl-1:2-di-hydroquinoxaline (XVI).*—Three grams of the quinoxaline compound (I), reduced to a fine powder, were stirred gradually into 10 c.c. of concentrated sulphuric acid cooled in a freezing mixture. The

compound dissolved with effervescence, carbon dioxide being evolved, to form a bright red solution. On pouring the acid solution into water, there was a slight precipitate of the yellow compound (XVII); this was filtered off, and the yellow filtrate neutralised with sodium carbonate, when the basic compound (XVI) was precipitated as an orange-red powder (2.5 grams). It is readily soluble in all the ordinary organic solvents with the exception of ether and light petroleum, in which it is very sparingly soluble, as it is also in water; the compound is dimorphous and crystallises from solution in any solvent in long, thin, red prisms that gradually redissolve when left in contact with the mother-liquor and are replaced by well-formed, octahedral prisms; each of the two forms melts at 135° (Found: C = 72.46; H = 5.78; N = 15.8; $M = 239$. $C_{16}H_{15}ON_3$ requires C = 72.47; H = 5.66; N = 15.8 per cent.; $M = 265$).

This compound, which is tasteless, forms soluble salts with mineral acids, yields a yellow, crystalline, sparingly soluble *chloroplatinate* (Found: Pt = 20.8. $C_{32}H_{32}O_2N_6Cl_6Pt$ requires Pt = 20.7 per cent.), and a *methiodide* that crystallises from alcohol and water in greenish-yellow, prismatic needles and melts at 205° (decomp.) (Found: I = 31.53. $C_{17}H_{15}ON_3I$ requires I = 31.2 per cent.). It is readily reduced by zinc and acetic acid, yielding a new base that crystallises from methyl alcohol in yellow prisms melting at $140-141^{\circ}$, and forms a sparingly soluble hydrochloride (Found: C = 72.07; H = 6.53; N = 15.8. $C_{15}H_{17}ON_3$ requires C = 71.87; H = 6.36; N = 15.8 per cent.).

3-Phenylmethylamino-2-keto-1-methyl-1:2-dihydroquinoxaline yields a *nitroso-derivative** that is soluble in all the ordinary organic solvents with the exception of ether and carbon tetrachloride, and crystallises in colourless, brilliant prisms melting at 197° (Found: C = 65.2; H = 4.8; N = 18.8. $C_{16}H_{11}O_2N_4$ requires C = 65.3; H = 4.76; N = 19.0 per cent.).

2. *Preparation of Derivatives of the Hexacyclic Ring Compound (XVII)* (6:8-Diketo-5:9-dimethyl-5:6:8:9-tetrahydromalonaldinium Hydroxide).—On the addition of about 0.5 c.c. of concentrated sulphuric acid to 0.3 gram of the quinoxaline compound (I), there was an immediate and vigorous reaction with evolution of a small quantity of carbon dioxide and the solution developed a bright red colour. The products of seven such experiments were poured into water, and the yellow precipitate (1.29 grams) was crystallised from

* 3-Phenylmethylamino-2-keto-1-methyl-1:2-dihydroquinoxaline does not contain an imino-group, and the nitroso-group probably replaces hydrogen in the para-position of the phenyl group; on the other hand, this compound gives the Liebermann reaction.

either (a) a mixture of chloroform and ethyl alcohol, from which 6 : 8-*diketo*-5 : 9-*dimethyl*-5 : 6 : 8 : 9-*tetrahydromalonalinium ethoxide* separated in pale yellow prisms melting at 240° (Found : C = 67.66; H = 5.66; N = 12.42. $C_{19}H_{19}O_3N_3$ requires C = 67.66; H = 5.64; N = 12.46 per cent.), or (b) a mixture of chloroform and methyl alcohol, from which 6 : 8-*diketo*-5 : 9-*dimethyl*-5 : 6 : 8 : 9-*tetrahydromalonalinium methoxide* separated in pale yellow prisms, m. p. 276–278° (Found : C = 66.9; H = 5.3. $C_{18}H_{17}O_3N_3$ requires C = 66.9; H = 5.3 per cent.).

The original yellow precipitate could not be purified, but after exhaustive extraction with boiling water it was found to be soluble in alkalis and to contain sulphur. Since on treatment with methyl and ethyl alcohols it yields the above described methoxide and ethoxide, respectively, which are insoluble in alkalis, it is probable that the yellow precipitate itself consists essentially of 6 : 8-*diketo*-5 : 9-*dimethyl*-5 : 6 : 8 : 9-*tetrahydromalonalinium sulphate*.

The acid filtrate from which the 1.29 grams of the yellow precipitate had been separated yielded 0.66 gram of the base, m. p. 135° (XVI), on treatment with sodium carbonate.

Preparation of 3 : 4-Oxido-2-keto-1-methyl-1 : 2 : 3 : 4-tetrahydropyrimidin-3-carboxymethyl-anilide (I) from the Potassium Salt of Nitromalondimethylanilide.

This was an attempt to prepare the quinoxaline compound (I) by the elimination of the elements of a molecule of water from the *aci*-form of nitromalondimethylanilide under similar conditions to those obtaining when the quinoxaline compound (I) is prepared from *isonitrosomalondimethylanilide* by the action of nitrosyl chloride and nitric acid. For this purpose, nitromalondimethylanilide was liberated from its salt in the presence of both nitric and nitrous acids.

To an intimate mixture of equal parts of powdered sodium nitrite with the potassium salt of nitromalondimethylanilide, suspended in dry chloroform, nitric acid (*d* 1.46) was added drop by drop, the mixture being well shaken and kept cool. There was a vigorous reaction at first and after it had subsided the mixture was warmed on the water-bath for a few minutes; water was then added to remove the sodium nitrate and excess of nitrite, and the chloroform layer separated and allowed to evaporate spontaneously. The residual syrup became crystalline on treatment with alcohol, and was found to consist of the quinoxaline compound (I), m. p. 191°, mixed with a small quantity of nitromalondimethylanilide, m. p. 156°.

Behaviour of Nitromalondimethylanilide and of its Potassium Derivative towards Concentrated Sulphuric Acid.

1. *Action of Concentrated Sulphuric Acid on Nitromalondimethyl-anilide.* Formation of 3:4-Oxido-2-hydroxy-1-methyl-1:4-dihydroquinoxaline (XVIII), and 3-Phenylmethylamino-2-keto-1-methyl-1:2-dihydroquinoxaline (XVI).—Four grams of finely powdered nitromalondimethylanilide were added in successive small portions to 30 c.c. of concentrated sulphuric acid. The solid dissolved, with the gradual development of a bright red colour, and carbon dioxide was evolved. The solution was warmed on the steam-bath for a few minutes and stirred until evolution of carbon dioxide ceased; it was then cooled and poured into water. The yellow compound (XVIII) thus precipitated weighed 1.4 grams and after crystallising twice from alcohol was obtained in bright yellow, thin prisms melting at 192–194° (Found: C = 61.5; H = 4.7; N = 16.2. $C_9H_8O_2N_2$ requires C = 61.4; H = 4.5; N = 15.9 per cent.). 3:4-Oxido-2-hydroxy-1-methyl-1:4-dihydroquinoxaline is tasteless. It is insoluble in sodium carbonate, but dissolves in sodium hydroxide solution.

The acid filtrate from which this compound had been separated yielded 0.4 gram of 3-phenylmethylamino-2-keto-1-methyl-1:2-dihydroquinoxaline (XVI) on neutralising with sodium carbonate. This exhibited the dimorphism characteristic of this compound, melted at 135°, and did not depress the melting point of an authentic specimen.

Two grams of the sodium salt of nitromalondimethylanilide, similarly treated with concentrated sulphuric acid, gave 0.6 gram of the compound (XVIII) and 0.1 gram of the compound (XVI).

We wish to thank the Council of the Royal Society for a grant which has defrayed much of the cost of this investigation; and the Advisory Council of the Scientific and Industrial Research Department for a maintenance grant to one of us (E. H. U.).

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Received, February 26th, 1923.

CXXII.—*The Conversion of Malonic Acid into d-Malic Acid.*

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ARISING from work which has been carried out on the optical activation of racemic acid by *l*-malic acid (McKenzie, T., 1915, **107**, 440; McKenzie and Walker, T., 1922, **121**, 349), it was considered desirable that the effect of *d*-malic acid should be examined in the same connexion. A convenient method for the preparation of the latter acid had first of all to be devised, and such a method is now described.

The reduction of *d*-tartaric acid by hydriodic acid gave, in the hands of Bremer (*Ber.*, 1875, **8**, 861, 1594), a malic acid with a dextrorotation. This method is useless for preparative purposes; in a careful study of it, Freudenberg (*Ber.*, 1914, **47**, 2027) has shown, by converting the crude acid into its methyl ester, that the yield amounted only to about 2 per cent., and evidence is also provided from the low value of the rotation of this ester that the action of the hydriodic acid is not unaccompanied by racemisation. In an investigation of much interest in those early days of stereochemistry, Bremer (*Ber.*, 1880, **13**, 351) resolved *r*-malic acid by cinchonine, obtaining in this manner a small quantity of ammonium hydrogen *d*-malate. No description of *d*-malic acid is, however, included in Bremer's account, and the method is unsuitable, so far as the experience of the present authors has gone.

Piutti (*Ber.*, 1886, **19**, 1691) has shown that *d*-asparagine undergoes conversion into *d*-malic acid by deamination with nitrous acid; but *d*-asparagine is a somewhat inaccessible compound. Again, Nef (*Annalen*, 1910, **376**, 37) was successful in obtaining 0.38 gram of *d*-malic acid by the oxidation of *d*- α -hydroxybutyrolactone with nitric acid; this specimen, which melted at 98–100°, gave $[\alpha]_D^{20} = +3.07$ in aqueous solution, whilst the sodium salt gave $[\alpha]_D^{20} = +8.29$ in the same solvent. Nef's work was confirmed later by Glatfield and Miller (*J. Amer. Chem. Soc.*, 1920, **42**, 2314), who quote 96° as the melting point of the acid, and give its rotation in aqueous solution as $[\alpha]_D^{20} = +3.46$. The purity of the acid as obtained by the American authors is thus deduced from the polarimetric values in aqueous solution, where the observed angles were necessarily rather small.

Walden (*Ber.*, 1896, **29**, 133, and subsequent papers), by the action of silver oxide and water on *d*-chloro- and *d*-bromo-succinic acids, obtained *d*-malic acid in admixture with its *r*-isomeride and

fumaric acid. The malic acid resulting from those actions can be separated from the fumaric acid by means of acetone or ethyl acetate, but, as happens so frequently in other cases also, the displacement of the halogen is invariably accompanied with racemisation, the extent of which depends on the experimental conditions. Mixtures of *r*- and *d*-malic acids have also come under the observation of Holmberg (*J. pr. Chem.*, 1913, [ii], 87, 473), but the separation of *d*- from *r*-malic acid by crystallisation of the mixture has never been successfully effected owing to the difficulty in the selection of a suitable solvent.

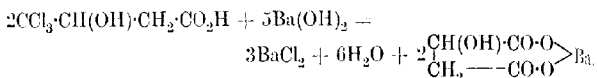
The most successful preparation of *d*-malic acid hitherto recorded is that described by Freudenberg and Brauns (*Ber.*, 1922, 55, [B], 1339). *d*-Tartaric acid was converted through its dimethyl ester into dimethyl monoacetyl-*d*-tartrate, in which the hydroxy-group was displaced by chlorine by means of thionyl chloride and pyridine. The acetyl group was then eliminated, and *d*-malic acid was obtained from the resulting chloromalic acid by reduction with zinc.

It is well known from the observations of Gernez and others that the addition of ammonium molybdate to an aqueous solution of *l*-malic acid causes the solution to become very strongly dextrorotatory. Darmon (*Compt. rend.*, 1920, 171, 318; 1921, 172, 1486), after examining the crystalline ammonium dimolybdo-*l*-malate, has recently, in conjunction with Périn (*Compt. rend.*, 1923, 176, 391), described the isolation of ammonium dimolybdo-*d*-malate, $C_4H_6O_5 \cdot 2MoO_3 \cdot 2NH_3$. This compound, which crystallises well, has the high levorotation $[\alpha]_{D}^{20} -220$, and can be prepared from the crude *d*-malic acid resulting from Walden's method. As it is stated that *d*-malic acid can be obtained from this molybdo-malate, it may emerge that, of the various methods hitherto quoted for preparing *d*-malic acid, this is the one most promising from the preparative point of view.

The method described in the present paper is based on the observation of Thurnlackh (*Monatsh.*, 1891, 12, 556) that 777-trichloro-3-hydroxybutyric acid can be converted into calcium *z*-malate by the action of alkali. The yield of calcium salt was small, and the *z*-malic acid was not isolated from it by Thurnlackh.

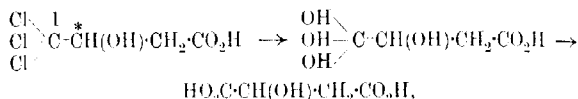
We employed pyridine with successful results in place of the glacial acetic acid used by Thurnlackh in the condensation of malonic acid with chloral, and found that the resulting 777-trichloro-3-hydroxybutyric acid crystallises from water with $1\frac{1}{2}H_2O$. This acid can readily be resolved into its optically active components by means of quinine in ethyl-alcoholic solution. The *l*-acid melts at 104–105°, has $[\alpha]_D^{20} = 29.6$ in ethyl-alcoholic solution ($c =$

1:5528), and gives barium *d*-malate on hydrolysis with barium hydroxide:



The preparation of the latter salt in good yield presented difficulties. On decomposition with oxalic acid it gave *d*-malic acid.

The preparation of *d*-malic acid by the method of Freudenberg and Brauns (*loc. cit.*) is of importance with respect to the configuration of the acid, since it is shown that *d*-tartaric acid and *d*-malic acid belong to the same steric series, and the work of Clough (T., 1918, 113, 526) on different lines was thus confirmed. The substitution of the $\text{--CO}_2\text{H}$ group for the --CCl_3 group in *l*- $\gamma\gamma\gamma$ -trichloro- β -hydroxybutyric acid would not be likely to cause configurative change if the mechanism of the displacement is interpreted on the simplest basis.



since, according to this scheme, C atom I remains throughout in direct attachment to the asymmetric carbon atom *, and no Walden inversion would then be possible. From this point of view, where the configurative relationship between the levorotatory chloro-acid and *d*-malic acid is concerned, it would probably be more correct to designate the levorotatory chloro-acid as *d*-, adopting *d*-malic acid as the reference compound. The nomenclature *l*-, which we have assigned to it, is based simply on the sign of the rotations observed in ethyl alcohol and acetone.

EXPERIMENTAL.

Resolution of $\gamma\gamma\gamma$ -Trichloro- β -hydroxybutyric Acid into its Optically Active Components.—The preparation of this racemic acid from malonic acid and chloral has been described by Thurnlackh (*loc. cit.*), who used glacial acetic acid as the condensing medium. This action proceeds in an irregular manner, sometimes failing altogether to give any of the desired product, as Auwers and Schmidt (*Ber.*, 1913, 46, 487) found. Doebner and Segelitz (*Ber.*, 1905, 38, 2733), however, give details for the condensation of ethyl malonic acid and chloral, when they found that pyridine can with advantage be substituted for glacial acetic acid in such actions. We therefore prepared the racemic acid as follows.

Pyridine (65 grams) was added gradually to a mixture of malonic acid (26 grams) and freshly-prepared chloral (37 grams). When the vigorous action had moderated, the mixture was heated on the water-bath for two hours to expel the carbon dioxide. The unattacked chloral together with the bulk of the pyridine was removed from the resulting oil by distillation under diminished pressure. The syrupy residue was then acidified with concentrated hydrochloric acid, water was added, and the crude chloro-acid extracted with ether. It can be crystallised from water without appreciable decomposition. At the ordinary temperature, it is sparingly soluble in water, from which it separates in glassy plates. When dried at the ordinary temperature, it melts at about 52–54°, and on analysis was found to contain $1\frac{1}{2}$ molecules of water of crystallisation. It becomes anhydrous when kept in an evacuated desiccator over sulphuric acid, and it then melts at 118–119°, whereas Thurnlackh (*loc. cit.*) gives 118.5°. The anhydrous acid may be crystallised conveniently from benzene. The average yield of this recrystallised anhydrous acid from four preparations conducted as above was 35.5 grams.

In the current number of the *Berichte*, the preparation of γ -trichloro- β -hydroxybutyric acid by the agency of pyridine is also described by Auwers and Wissebach (*Ber.*, 1923, 56, [B], 715).

The ethyl ester separates from benzene in silky prisms, and melts at 57–58° in agreement with the value 56–57° observed by Auwers and Schmidt (*loc. cit.*).

The resolution of the acid proceeds very smoothly, and the following is a description of a typical preparation. Ninety-one grams of quinine (1 mol.) were dissolved by heating with 600 c.c. of ethyl alcohol, and 50 grams of the anhydrous acid (1 mol.) were added. Solution of the acid took place with readiness. On cooling, crystallisation started quickly, and after one day in the ice-chest, the resulting solid was crystallised from 1200 c.c. of ethyl alcohol. The quinine *l*-salt (59 grams) separated in glassy prisms, which melt with decomposition at about 208°. At 25.9°, 100 c.c. of its ethyl-alcoholic solution contain 0.44 gram of salt. After the salt was decomposed by dilute sulphuric acid, the chloro-acid was extracted with ether. The yield amounted to 19 grams, and after two crystallisations from benzene the acid (16.5 grams) was pure.

In another resolution, where 50 grams of the *r*-acid were again employed, the quinine salt was crystallised from alcohol five times, and the resulting acid crystallised three times from benzene. The optical activity of the acid was the same as before, and therefore the prolonged crystallisation of the quinine salt is not necessary.

l- γ -Trichloro- β -hydroxybutyric acid melts at 104–105°. It is

readily soluble in ethyl alcohol and in acetone at the ordinary temperature. It is readily soluble in hot benzene, and sparingly soluble in the cold solvent, from which it separates in glassy, hexagonal prisms. It is sparingly soluble in cold toluene, chloroform, or light petroleum (b. p. 40–60°). It is much more soluble in water than is the inactive isomeride, and it differs from the latter in not crystallising with water of crystallisation (Found: C = 23.2; H = 2.3. Calc., C = 23.1; H = 2.4 per cent.). Its specific rotation was determined as follows:

In ethyl alcohol:

$$l = 2, c = 1.5528, \alpha_D^{25} = -0.92^\circ, \text{whence } [\alpha]_D^{25} = -29.6^\circ.$$

$$l = 2, c = 4.0004, \alpha_D^{25} = -2.41^\circ, \text{whence } [\alpha]_D^{25} = -30.1^\circ.$$

$$l = 2, c = 4.0004, \alpha_D^{15} = -2.77^\circ, \text{whence } [\alpha]_D^{15} = -34.6^\circ.$$

In acetone:

$$l = 2, c = 1.553, \alpha_D^{25} = -0.70^\circ, \text{whence } [\alpha]_D^{25} = -22.5^\circ.$$

$$l = 2, c = 1.553, \alpha_D^{15} = -0.78^\circ, \text{whence } [\alpha]_D^{15} = -25.1^\circ.$$

In the preceding resolution, the first filtrate, after the removal of the crystals containing a preponderance of the *l*BdA salt, gave on partial evaporation 26 grams of crystals in which the *l*BdA salt was in excess. The acid from this amounted to 8.5 grams which, when crystallised three times from benzene, gave 5 grams of the pure *d*-acid (Found: Cl = 51.4. Calc., Cl = 51.3 per cent.). *d*- $\gamma\gamma$ -Trichloro- β -hydroxybutyric acid gave values for its specific rotation in agreement with those for the *l*-isomeride.

In ethyl alcohol:

$$l = 2, c = 1.551, \alpha_D^{25} = +0.87^\circ, \text{whence } [\alpha]_D^{25} = +28^\circ.$$

$$l = 2, c = 1.551, \alpha_D^{15} = +1.08^\circ, \text{whence } [\alpha]_D^{15} = +34.8^\circ.$$

In acetone:

$$l = 2, c = 1.5528, \alpha_D^{25} = +0.71^\circ, \text{whence } [\alpha]_D^{25} = +22.9^\circ.$$

$$l = 2, c = 1.5528, \alpha_D^{15} = +0.81^\circ, \text{whence } [\alpha]_D^{15} = +26.1^\circ.$$

Conversion of l- $\gamma\gamma$ -Trichloro- β -hydroxybutyric Acid into d-Malic Acid.—It was found that the *l*-chloro-acid on decomposition with potassium hydroxide, and the subsequent addition of barium chloride, gave a dextrorotatory barium salt. Under the conditions adopted, the latter salt was not quite pure barium *d*-malate; in one case, for example, the percentage of barium in the anhydrous salt was 50.5 (Calc., 51.0). 0.2351 Gram was decomposed by 1.54 c.c. of dilute hydrochloric acid containing the calculated amount of acid. 3.95 C.c. of potassium hydroxide (0.3132N) were added, and then 6.04 c.c. of a standard solution of uranium nitrate (32.9356

grams of the hydrated salt in one litre of water). The solution, when made up to 20 c.c. with water, gave $\alpha_D + 2.30^\circ$ ($l = 2$), whereas barium *l*-malate, prepared from Kahlbaum's acid, gave, under similar conditions, a higher value, namely $\alpha_D + 2.66^\circ$. In several other cases the percentage of barium was 50.2, 49.3, 50.2, respectively, whilst the malic acid obtained from those products apparently contained some of the *r*-acid. Slight racemisation had most likely taken place by the agency of the potassium hydroxide, which was used in strong solution for the elimination of chlorine from the chloro-acid (compare McKenzie and Thompson, T., 1905, 87, 1004). The decomposition of the *l*-chloro-acid by potassium hydroxide and the subsequent addition of barium chloride, did not therefore prove to be satisfactory for the preparation of barium *d*-malate. It seems to be difficult to wash the product free from potassium chloride without considerable loss. Moreover, barium *d*-malate tends to form supersaturated solutions, and we could not depend on the polarimetric results, even with such solutions, as a criterion of purity, as the observed angles of rotation are too small (compare Schneider, *Annalen*, 1881, 207, 277). Recourse was accordingly had to the uranyl reagent in order to enhance the rotations. The use of potassium hydroxide was therefore abandoned, and the chloro-acid was acted on by barium hydroxide as follows. An aqueous solution of barium hydroxide (824.5 c.c.) containing the calculated quantity of the alkali was added within an interval of half an hour to 9.98 grams of the *l*-chloro-acid. The volume of the solution in the flask was then reduced to 450 c.c. by evaporation on the water-bath, for ten hours, in the absence of carbon dioxide. The elimination of the halogen was then complete, and on evaporation to smaller bulk the barium salt crystallised. This was removed and washed to free completely from chloride. Yield 9.3 grams. For analysis, it was dried at 120° (Found: Ba = 51.1. Calc., Ba = 51.0 per cent.). The salt was pure barium *d*-malate. 0.2358 Gram was employed with the uranyl reagent in the proportions already quoted. Found: $\alpha_{5461} + 3.15^\circ$ ($l = 2$). A specimen of pure barium *l*-malate gave, under similar conditions, $\alpha_{5461} + 3.20^\circ$ ($l = 2$).

Barium *d*-malate (8.73 grams) was suspended in water and treated with the calculated amount of oxalic acid. After the removal of the barium oxalate, the filtrate was evaporated to small bulk, and dried in a desiccator over sulphuric acid. The crude malic acid (4 grams) was purified by dissolving in acetone and precipitating with xylene. It then melted at $99-99.5^\circ$, whereas *l*-malic acid melts at 100° (Walden, *Ber.*, 1896, 29, 1699). Yield, 2.5 grams. It was free from fumaric acid, as it did not decolorise cold alkaline

potassium permanganate. Its silver salt on analysis gave Ag = 61.8 per cent. (Calc., 62.0).

0.2233 Gram was mixed with 0.5152 gram of ammonium molybdate, and made up to 20 c.c. with water. Found: $\alpha_D^{45} = -12.29^\circ$ ($l = 2$), whence $[\alpha]_D^{45} = -550^\circ$. A specimen of the pure *l*-acid gave, under similar conditions, $[\alpha]_D^{55} = +12.69^\circ$ ($l = 2$), whence $[\alpha]_D^{55} = +568^\circ$.

In another experiment, 6.5 grams of barium *d*-malate yielded 3.04 grams of *d*-malic acid. 0.279 Gram of this acid was mixed with 0.6438 gram of ammonium molybdate, and made up to 25 c.c. with water. Found: $\alpha_D^{45} = -12.46^\circ$ ($l = 2$), whence $[\alpha]_D^{45} = -558^\circ$. Its silver salt on analysis gave Ag = 61.8 per cent. (Calc., 62.0).

One of us (H. J. P.) desires to express his best thanks to the Department of Scientific and Industrial Research for a grant which enabled him to take part in this investigation.

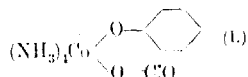
UNIVERSITY COLLEGE, DUNDEE.
UNIVERSITY OF ST. ANDREWS.

[Received, April 7th, 1923.]

CXXIII.—*Researches on Residual Affinity and Coordination. Part XVI. Normal and Acid Salicylatotetramminocobaltic Salts.*

By GILBERT T. MORGAN and J. D. MAIN SMITH.

IN a former communication on cobaltamines (T., 1922, 121, 1956), we described the preparation of a new series of co-ordinated compounds containing salicylic acid implicated in a univalent tetramminocobaltic radicle having the following chemical constitution:



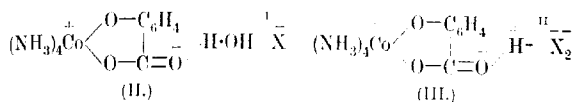
We showed further that this univalent radicle has the following outstanding properties:

(1) It resembles the ions of the alkali metals, and particularly that of sodium. Those reagents which precipitate sodium from its soluble salts yield sparingly soluble salts of the salicylatotetramminocobaltic complex.

(2) In its normal salts this cobaltamine radicle exists in a hydrated form—one molecule of combined water to each molecule of the ion. This water is held tenaciously up to 135° and its removal is attended by destruction of the complex.

(3) The salicylatocobaltamine complex has a marked tendency to form acid or hydrogen salts, in which it exists in an anhydrous condition.

The last two characteristics of the salicylatotetrammine complex were explained by assuming that it contains two foci of co-ordination, a positive focus due to the trivalent cobalt atom and a negative focus attributable to an oxygen atom and probably to that oxygen which is present in the carbonyl radicle. In the normal salts, this oxygen atom attracts the firmly-held water molecule, bringing it into the co-ordination complex as in formula II; in the hydrogen salts, it co-ordinates with the hydron as in formula III.



The oxygen atom acting as the negative co-ordinating focus retains its bivalency, but assumes the co-ordination number 3 as in the large and varied group of oxonium salts and as in such aquo-salts as aquopentamminocobaltic chloride (roseocobaltic chloride) and its numerous analogues. In the foregoing formulæ, the symbol X expresses any univalent acidic radicle which is united by an electrovalency with the positive cobalt atom. X₂ may be either two univalent acidic radicles or one bivalent acidic radicle.

These properties which stamp the salicylatotetramminocobaltic radicle as a binuclear co-ordination complex of mixed polarity are sufficiently remarkable to warrant a more comprehensive study of its derivatives, and this investigation has now been completed by an examination of forty-seven salts of the new cobaltamine.

I. The Salicylatotetramminocobaltic Complex as a Compound Alkali-ion Resembling Sodium.

It was shown in the earlier paper that the salicylatocobaltamine resembles sodium in yielding the following sparingly soluble salts: oxalate, bicarbonate, and α -naphthylamine-8-sulphonate. This analogy has now been confirmed by the preparation of the very insoluble *salicylatotetramminocobaltic pyroantimonate* (IV), *dihydroxytartrate*, [R . . . H₂O]₂:C₄H₄O₈, and *acid oxalate* (VIII), and the moderately soluble *mesoxalate*, [R . . . H₂O]₂:C₃H₂O₆.2H₂O. The first two of these new salts correspond with the two well-known tests for sodium with pyroantimonate and with Fenton's reagent (T., 1898, 73, 72). It was found, however, that Ball's reagent for sodium (T., 1909, 95, 2128), potassium cesium bismuthonitrite, failed to give a precipitate with *salicylatotetramminocobaltic nitrite* (V).

These results may be summarised by stating that in seven cases out of the eight examined the new cobaltammine resembles sodium in the formation of analogous sparingly soluble salts.

II. The Hydrated and Anhydrous Conditions of the Salicylato-tetramminocobaltic Complex.

The foregoing analogy between sodium and the salicylatocobaltammine also extends to the properties of certain of their soluble normal salts as, for example, the halide salts (*ibid.*, p. 1957), but it breaks down completely in reference to the property of forming stable acid or hydrogen salts, which is possessed in a far greater degree by the cobaltammine than by the alkali metal. Twenty-five normal salts of this base have been examined, and in every case one molecule of firmly held water is present for each molecule of the complex cation. In many instances, the anion is also hydrated, but this water is generally removable, either at 100° or even at lower temperatures.

In the earlier experiments all the acid or hydrogen salts then examined with the exception of the bisulphite were anhydrous, and accordingly this exception was regarded as a normal salt of monobasic sulphurous acid. This formulation (*ibid.*, p. 1958) requires amendment in the light of further research. The hydrogen sulphate and hydrogen dithionate are both hydrated, although less so than the corresponding normal salts (p. 1105), and this hydrated character of acid salts of other sulphur oxy-acids suggests that the bisulphite may also be an acid salt with its water associated with the anion $[R \dots H]SO_3 \cdot H_2O$. But, on the other hand, it was not found possible to isolate the normal sulphite.

Altogether twenty-two acid or hydrogen salts have been examined and of these eleven are completely anhydrous and of the remainder, five, although containing water, are less hydrated than the corresponding normal salts. In the *hydrogen dibromide*, $[R \dots H]Br_2 \cdot H_2O$, the amount of water is the same (1 mol.) as in the normal bromide, but the former loses its water at 75°, whereas the latter retains its water at 135°, and only loses it with destruction of the co-ordination complex. The *hydrogen dichloride* (formula XII) is exceptional in containing twice as much water (2H₂O) as the normal chloride, but all the water of the former salt is expelled at 100°, whereas the latter retains its hydrated character at 135°. The acid cobalticyanide (XIV) has only slightly less water than the normal salt, but is entirely deprived of it at 97°, whereas the latter compound is still hydrated at 130°.

Sixteen pairs of normal and acid salts have been obtained, the states of hydration of which are summarised in the following tabula-

tion. In all cases throughout this paper the symbol R denotes the anhydrous cobaltammine complex of formula I.

Salicylatotetramminocobaltic

Combined acid.	Normal salt.	Acid or hydrogen salt.
Carbonic acid	$[R \dots H_2O]_2CO_3 \cdot H_2O$	$[R \dots H]CO_2$
Oxalic	$[R \dots H_2O]_2C_2O_4$	$[R \dots H]C_2O_4$
Silicofluoric	$[R \dots H_2O]_2SiF_6 \cdot 2H_2O$	$[R \dots H]SiF_6$
Nitric	$[R \dots H_2O]NO_3 \cdot 2H_2O$	$[R \dots H](NO_3)$
Phosphorous	$[R \dots H_2O]_2HPO_3 \cdot 2H_2O$	$[R \dots H]HPO_3 \cdot 2H_2O$
Pyrophosphoric	$[R \dots H_2O]_4P_2O_5 \cdot 14H_2O$	$[R \dots H]_2P_2O_5 \cdot 4H_2O$
Sulphuric	$[R \dots H_2O]_2SO_4 \cdot 2H_2O$	$[R \dots H]SO_4 \cdot 2H_2O$
Dithionic	$[R \dots H_2O]_2S_2O_6 \cdot 2H_2O$	$[R \dots H]S_2O_6 \cdot H_2O$
Tetrathionic	$[R \dots H_2O]_2S_4O_{10}$	$[R \dots H]S_4O_{10}$
Hydrochloric	$[R \dots H_2O]Cl$	$[R \dots H]Cl \cdot 2H_2O$
Hydrobromic	$[R \dots H_2O]Br$	$[R \dots H]Br \cdot H_2O$
Chloroplatinic	$[R \dots H_2O]_2PtCl_6 \cdot 2H_2O$	$[R \dots H]PtCl_6 \cdot H_2O$
Cobalticyanic	$[R \dots H_2O]_2Co(CN)_6 \cdot 1.5H_2O$	$[R \dots H]_2Co(CN)_6 \cdot 4H_2O$
<i>Mercurihalides (XIII.)</i>		
Mercurichloride	$[R \dots H_2O]_2Hg_2Cl_4$	$[R \dots H]Hg_2Cl_4$
Mercuribromide	$[R \dots H_2O]_2Hg_2Br_4$	$[R \dots H]Hg_2Br_4$
Mercuri-iodide	$[R \dots H_2O]_2Hg_2I_4$	$[R \dots H]Hg_2I_4$

III. Hydrogen Salts of Unstable Acids.

Owing to the presence of two co-ordinating foci in the salicylatocobaltammine complex this salt-forming cation exhibits in a marked degree the property of producing hydrogen salts which is demonstrated in the foregoing table.

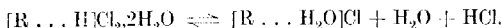
It has been stated that "Von der Kieselfluorwasserstoffsäure kennen wir nur normale Salze" (Ephraim, "Anorganische Chemie," 1922, p. 614). Similar statements occur in the literature regarding the non-existence of acid dithionates and tetrathionates (Roscoe and Schorlemmer, "Inorganic Chemistry," I, 1920, p. 499). These three acids, H_2SiF_6 , $H_2S_2O_6$, and $H_2S_4O_{10}$, have, however, yielded definitely stable hydrogen salts with the salicylatocobaltammine.

The explanation of this noteworthy property of the new cobaltammine lies undoubtedly in the circumstance that it contains a subsidiary focus of co-ordination due to oxygen. The foregoing tabulated stable hydrogen salts of unstable acids are in reality oxonium salts and owe their permanence to the implication of the hydron in the binuclear co-ordination sphere.

Unsuccessful attempts were made to obtain the hydrogen salts of nitrous and thiosulphuric acids, but even oxonium salt formation was insufficient to ensure the permanence of the readily dehydrated HNO_2 group or the very unstable HS_2O_3 radicle.

The hydrogen salts of the more stable acids tabulated above have interesting properties, and especially the *dihydrated hydrogen dichloride* (formula XII), which on treatment with water or aqueous

pyridine loses half its water and chlorine-ion with precipitation of the less soluble normal chloride:

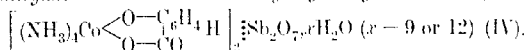


The other hydrogen salts, with the exception of the bicarbonate, manifest their oxonium character in a similar way by dissolving in water to strongly acid solutions, thus showing that the foregoing equation represents a general reversible chemical change.

EXPERIMENTAL.

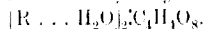
I. Sparingly Soluble Salts of the Salicylatotetramminocobaltic Radical.

Salicylatotetramminocobaltic Dihydrogen Pyroantimonate,



—The normal salicylatotetramminocobaltic bromide (7.22 grams) was triturated for one hour with 20 c.c. of water and 7 grams of silver pyroantimonate. The solution obtained from the silver bromide by four extractions with successive 20 c.c. of hot water was cooled and treated with alcohol and acetone, when a glistening, finely crystalline, pink powder separated, the yield being 62 per cent. The air-dried product was sparingly soluble in water to a faintly acidic pink solution, giving no precipitate with sodium salts, but yielding white antimonie acid on adding acetic acid (Found: Co = 10.7; NH_3 = 12.3. The dodecahydrate requires Co = 10.8; NH_3 = 12.4 per cent.). After drying for ten days over calcium chloride under reduced pressure, the weight became constant (Found: Co = 11.4; NH_3 = 13.2; Sb = 22.4. The ennecahydrate requires Co = 11.3; NH_3 = 13.1; Sb = 23 per cent.). This lower hydrate lost half its water after seven hours at 100°.

Salicylatotetramminocobaltic Dihydroxytartarate,



—One gram of dihydroxytartaric acid, dissolved in 5 c.c. of water, was added slowly to 3.5 grams of the normal tetramminocarbonate in 11 c.c. of warm water, when the dihydroxytartarate separated in small, damask-red plates sparingly soluble in water to a red solution which gave only a slight turbidity with sodium salts. This solution reduced cold ammoniacal silver nitrate and hot solutions of mercurous and mercuric chlorides; it gave no violet coloration with ferrie chloride either with or without addition of hydrogen peroxide (Found: Co = 16.0; NH_3 = 18.4. The dihydrate requires Co = 15.9; NH_3 = 18.3 per cent.).

Salicylatotetramminocobaltic Mesocate, $[\text{R} \dots \text{H}_2\text{O}]_2 \text{C}_3\text{H}_2\text{O}_6 \cdot 2\text{H}_2\text{O}$.

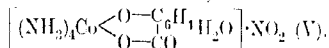
—Violet-red, rhomboidal plates of the tetrahydrated salt separated

slowly on cooling when acetone-alcohol (1:1) was added to the filtrate from a mixture of 4.4 grams of the tetrammine chloride, and 2.5 grams of silver mesoxalate in 15 c.c. of water at 40°. The yield of air-dried product was 86 per cent. (Found: Co = 16.2; NH_3 = 18.6. The tetrahydrate requires Co = 16.1; NH_3 = 18.6 per cent.).

Owing to its extreme solubility in water and organic solvents the hydrogen mesoxalate could not be isolated from the interaction of silver mesoxalate and tetrammine hydrogen dichloride; only a red, vitreous mass was obtainable on evaporation over calcium chloride.

II. Hydrated Normal Salts of the Salicylatotetramminocobaltic Series.

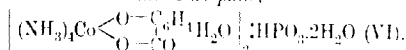
Salicylatotetramminocobaltic Nitrite.



—Clusters of glistening, dark purplish-red, pointed leaflets were precipitated on adding a mixture of alcohol, acetone, and ether to the deep red filtrate from 14.4 grams of the normal tetrammine bromide, 7 grams of silver nitrite, and 15 c.c. of water (yield 50 per cent.). This crystalline product was stable in air and very soluble in water to a deep red solution which gave no precipitate with "nitron" acetate, but readily diazotised aniline hydrochloride (Found: Co = 17.8; NH_3 = 20.7; N as NO_2 = 4.3. The monohydrate requires Co = 18.0; NH_3 = 20.8; N as NO_2 = 4.3 per cent.).

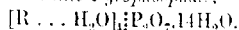
Nitrous fumes were instantly evolved on attempting to prepare the hydrogen dinitrite from the tetrammine-hydrogen dichloride and silver nitrite; the only product isolated was the foregoing normal nitrite.

Salicylatotetramminocobaltic Phosphite.



—The tetrammine bicarbonate (6.5 grams) dissolved in 8 c.c. of 5N-phosphorous acid to a blood-red solution from which alcohol and ether precipitated a dark red oil which crystallised slowly to a mass of damask-red plates (yield 51 per cent.). This salt was stable in air and extremely soluble in water; the deep red solution reducing ammoniacal silver nitrate and converting mercuric into mercurous chloride (Found: Co = 16.9; NH_3 = 19.9; P = 4.4; H_2O at 100° = 4.9. The tetrahydrate requires Co = 17.4; NH_3 = 20.1; P = 4.6; $2\text{H}_2\text{O}$ = 5.3 per cent.). The remaining water is held tenaciously as in the other normal salts.

Salicylatotetramminocobaltic Pyrophosphate.

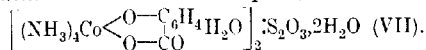


—The normal tetrammine chloride (8.86 grams) was triturated for

one hour with a 50 per cent. excess of silver pyrophosphate (6.5 grams) and 12 c.c. of water. Addition of alcohol, ether, and acetone to the filtrate and washings from silver chloride produced a heavy, dark red oil which, after stirring for two hours, crystallised to a mass of damask-red, elongated, rhomboidal plates (yield 66 per cent.). The product, which was recrystallised from dilute alcohol, was somewhat sparingly soluble in water, its aqueous solution giving with silver nitrate a white precipitate of silver pyrophosphate (Found: Co = 15.3; NH₃ = 17.6; P = 4.0; H₂O at 98° = 16.1. The octodecahydrate requires Co = 15.2; NH₃ = 17.6; P = 4.0; 14 H₂O = 16.3 per cent.). The remaining four molecular proportions of water are held tenaciously.

Ferric pyrophosphate dissolved in a solution of the foregoing pyrophosphate in proportions corresponding with the double salt Na₄Fe₂(P₂O₇)₃·7H₂O (Oliveri-Mandalà, *Gazzetta*, 1921, 51, i, 130), but no crystalline cobaltamine analogue of this sodium salt could be isolated, only a red vitreous mass being obtained on evaporation.

Salicylatotetramminocobaltic Thiosulphate,



—The filtrate from the trituration of 1.6 grams of barium thiosulphate monohydrate and 4.2 grams of tetrammine sulphate in 10 c.c. of warm water was cooled on ice, when a silky, dark red precipitate separated (yield 75 per cent.), which was recrystallised from hot dilute alcohol in violet-red, rhomboidal plates moderately soluble in water to a dark red solution, from which acids liberated sulphur and sulphur dioxide (Found: Co = 16.6; NH₃ = 19.3; S₂O₃ = 15.5; H₂O at 100° = 5.1. The tetrahydrate requires Co = 16.6; NH₃ = 19.2; S₂O₃ = 15.8; 2H₂O = 5.1 per cent.).

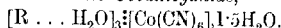
Salicylatotetramminocobaltic Dithionate, [R...H₂O]₂·S₂O₆·2H₂O.—Seven grams of tetrammine sulphate and 3.35 grams of dihydrated barium dithionate were mixed in hot aqueous solution (90 c.c.); the filtrate on cooling deposited large, sparingly soluble, brilliant violet, rhomboidal plates (yield 74 per cent.) (Found: Co = 15.7; NH₃ = 17.8; H₂O at 100° = 4.8. The tetrahydrate requires Co = 15.6; NH₃ = 17.9; 2H₂O = 4.7 per cent.).

In the two foregoing salts the tenaciously held water is presumably associated with the cobaltamine cation.

Salicylatotetramminocobaltic Tetrathionate. [R...H₂O]₂·S₄O₆.—The tetrammine bicarbonate (8.1 grams) dissolved in 35 c.c. of 0.75*N*-tetrathionic acid to a dark red solution from which violet-red, elongated, rhomboidal plates separated in 57 per cent. yield on adding a few c.c. of acetone; the product is moderately soluble in

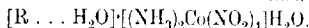
cold water (Found: Co = 14.8; NH_3 = 17.3; S = 16.1. The dihydrate requires Co = 15.0; NH_3 = 17.3; S = 16.3 per cent.).

Salicylatotetramminocobaltic Cobalticyanide,



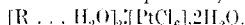
—The tetrammine bicarbonate (4.81 grams) was dissolved in 8.3 c.c. of 1.8*N*-cobalticyanic acid; the solution was treated with alcohol, acetone, and ether until a heavy, brown oil separated; this, after prolonged rubbing, crystallised to a purplish-red mass which was recrystallised from warm water (yield 40 per cent.). This product consisted of clusters of violet-red, glistening plates often of acicular habit and extremely soluble in water [Found: Co = 22.0; NH_3 = 18.8; H_2O = 2.5. The hydrated salt ($4\frac{1}{2}\text{H}_2\text{O}$) requires Co = 21.7; NH_3 = 18.8; $1\frac{1}{2}\text{H}_2\text{O}$ = 2.5 per cent.].

Salicylatotetramminocobaltic Diamminocobaltinitrite,



—The tetrammine bromide (3.85 grams) and 3.6 grams of silver diamminocobaltinitrite (from Erdmann's salt) were triturated in 15 c.c. of water. The reddish-brown filtrate from silver bromide deposited slowly golden-brown, rhomboidal plates, yellow by transmitted light (yield 45 per cent.). The product was moderately soluble to a reddish-brown solution from which mercurous nitrate precipitated yellow prisms of mercurous diamminocobaltinitrite (Found: Co = 20.4; NH_3 = 17.7; N as NO_2 = 9.6. The dihydrate requires Co = 20.5; NH_3 = 17.7; N as NO_2 = 9.7 per cent.).

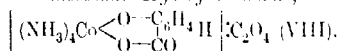
Salicylatotetramminocobaltic chloroplatinate,



—The tetrammine bicarbonate was dissolved in an equivalent amount of *N*/20-chloroplatinic acid, when tufts of small, reddish-brown needles separated, changing subsequently to clusters of elongated, six-sided plates (yield 70 per cent.) (Found: Co = 11.9; Pt = 19.4; H_2O at 100° = 3.5. The tetrahydrate requires Co = 11.7; Pt = 19.4; $2\text{H}_2\text{O}$ = 3.6 per cent.). The product was moderately soluble to a red solution from which dilute hydrochloric acid precipitated the brown acidic or hydrogen chloroplatinate (XV).

III. Hydrogen Salts of the Salicylatocobaltammine Series.

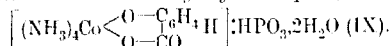
Salicylatotetramminocobaltic Hydrogen Oxalate,



—The salicylatocobaltammine bicarbonate (4.86 grams) was dissolved in 15 c.c. of hot water containing 1.9 grams of crystallised oxalic acid; an alcohol-acetone-ether mixture was added until the pink precipitate remained which rapidly became crystalline. The

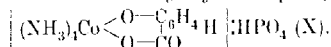
liquid was warmed to redissolve this product, acetone was added, and the solution cooled on ice. The sparingly soluble hydrogen oxalate separated in clusters of bright scarlet plates, the yield being 57 per cent. (Found: Co = 16.6; NH₃ = 19.2; C₂O₄ = 25.1. The anhydrous salt requires Co = 16.8; NH₃ = 19.3; C₂O₄ = 25.0 per cent.).

Salicylatotetramminocobaltic Hydrogen Phosphite,



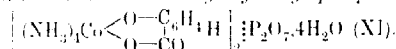
—The bicarbonate (3.24 grams) dissolved to a blood-red solution in 8 c.c. of 5*N*-phosphorous acid (1.64 grams H₃PO₃) from which alcohol and ether precipitated a dark red oil which slowly became crystalline (yield 47 per cent.). The product consisted of irregular, dark red plates, extremely soluble in water to a red solution which was acid to phenolphthalein but not to methyl-orange or bromo-phenol-blue. The solution reduced ammoniacal silver nitrate and converted mercuric into mercurous chloride (Found: Co = 15.7; NH₃ = 17.8; P = 8.2. The dihydrate requires Co = 15.7; NH₃ = 17.9; P = 8.2 per cent.).

Salicylatotetramminocobaltic Dihydrogen Phosphate,



—Excess of the bicarbonate (14.58 grams) was dissolved in 3.75 c.c. of 24*N*-phosphoric acid (2.94 grams H₃PO₄) and 25 c.c. of water and warmed to about 60°. Carbon dioxide was evolved and, on cooling, the dark red solution deposited glistening, pink, elongated, rhomboidal plates and flattened needles, the yield being 93 per cent. (Found: Co = 16.2; NH₃ = 18.8; P = 8.5. The anhydrous salt requires Co = 16.4; NH₃ = 18.9; P = 8.6 per cent.). The dihydrogen phosphate was only moderately soluble in water to a red solution which was neutral to methyl-orange and acid to litmus.

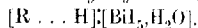
Salicylatotetramminocobaltic Dihydrogen Pyrophosphate,



—When 5.83 grams of bicarbonate were dissolved in 15 c.c. of pyrophosphoric acid solution (from 6.0 grams of silver pyrophosphate and 1.46 grams of hydrogen chloride in 14 c.c. of water), the normal pyrophosphate first crystallised out and then redissolved to a blood-red solution from which alcohol-acetone precipitated a heavy, brownish-red oil. This product was stirred with 50 c.c. of alcohol for three hours, when crystallisation set in. The dihydrogen pyrophosphate was then obtained in pale rose pink, irregular plates, dissolving readily in water to a bright red, strongly acid solution from which silver nitrate precipitated white silver pyrophosphate

(Found: Co = 15.6; NH_3 = 17.7; P = 8.2; H_2O at 100° = 8.6. The tetrahydrate requires Co = 15.3; NH_3 = 17.6; P = 8.0; $4\text{H}_2\text{O}$ = 9.3 per cent.).

Salicylatotetramminocobaltic Hydrogen Bismuthiodide,



—The carbonate (1.6 grams) dissolved in 2.5 c.c. of colourless 4N-hydriodic acid (\equiv 1.28 grams HI) and the solution was treated with 15 c.c. of aqueous potassium iodide containing 7.55 grams of potassium bismuthiodide and 1 c.c. of hydriodic acid. A flocculent, orange precipitate separated which became brown and granular and then changed suddenly to glistening, chocolate-brown needles which were washed successively with a hydriodic acid solution of potassium iodide and light petroleum (yield 90 per cent.) (Found: Co = 5.2; NH_3 = 6.0; Bi = 18.8; H_2O = 1.5. The monohydrated bismuthiodide requires Co = 5.2; NH_3 = 6.0; Bi = 18.5; H_2O = 1.6 per cent.).

The brown, elongated, six-sided plates, which were brownish-red by transmitted light, were decomposed by water to an orange acid solution and a brown precipitate of bismuth iodide, changing on dilution to yellow bismuth oxyiodide.

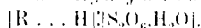
Salicylatotetramminocobaltic Hydrogen Sulphate,



—The cobaltammine bicarbonate (32.4 grams), when dissolved in 5 c.c. of water and 4.9 grams of concentrated sulphuric acid, yielded a purple-red, crystalline precipitate of the normal sulphate. This salt redissolved on the further addition of 4.9 grams of concentrated sulphuric acid and crystallisation of the hydrogen sulphate was promoted by introducing a few drops of alcohol (yield 50 per cent.). The product, which consisted of bright brick-red, micaceous plates, pink by transmitted light, was stable in air, losing water very slowly at 100° (Found: Co = 14.9; NH_3 = 17.0; SO_4 = 24.3. The dihydrate requires Co = 14.9; NH_3 = 17.2; SO_4 = 24.2 per cent.).

The hydrogen sulphite dissolved in water to a bright red, strongly acid solution turning to violet-red on adding alkalis.

Salicylatotetramminocobaltic Hydrogen Dithionate,

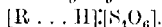


—The cobaltammine bicarbonate (3.24 grams) dissolved in 12.5 c.c. of 0.8N-dithionic acid (\equiv 0.81 grams $\text{H}_2\text{S}_2\text{O}_6$) to a purple-red liquid which set immediately to a violet-red paste of the normal dithionate. This precipitate dissolved to a bright red solution on a further addition of 12.5 c.c. of 0.8N-dithionic acid. The hydrogen dithionate separated in bright red plates on adding alcohol, the yield being 88 per cent. (Found: Co = 13.4; NH_3 = 15.4; S = 14.3.

The monohydrate requires Co = 13.4; NH₃ = 15.4; S = 14.5 per cent.).

This hydrogen dithionate was obtained from water in glistening, red, elongated, rectangular plates and from hot dilute alcohol in bronzy-violet prisms, blood-red by transmitted light. Approximately one-twelfth of the water of hydration was removed after four hours at 100°.

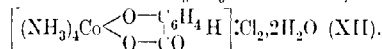
Salicylatotetramminocobaltic Hydrogen Tetrathionate,



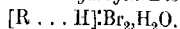
—The cobaltammine bicarbonate (4.86 grams) dissolved in 21 c.c. of 0.75*N*-tetrathionic acid (\equiv 1.6 grams H₂S₄O₆) to a dark red solution from which bright red plates separated on a further addition of 21 c.c. of the tetrathionic acid solution (yield 85 per cent.) (Found: Co = 12.1; NH₃ = 14.0; S = 26.5. The anhydrous salt requires Co = 12.1; NH₃ = 13.9; S = 26.2 per cent.).

This hydrogen tetrathionate consisted of brilliant red, elongated, rhomboidal, and six-sided plates sparingly soluble in water to a bright red, strongly acid solution, becoming violet-red with alkalis.

Salicylatotetramminocobaltic Hydrogen Dichloride,

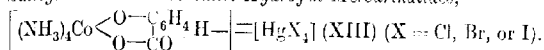


—A thin, purple paste, formed on adding 9.72 grams of the cobaltammine bicarbonate to 15 c.c. of 2*N*-hydrochloric acid, redissolved to an intensely red solution on introducing another equal proportion of acid. From this solution nothing could be precipitated by concentrated hydrochloric acid or by alcohol or acetone, but on adding a mixture of one volume of alcohol, three volumes of dry acetone, and two of dry ether, a heavy, brown oil resembling bromine separated which on stirring suddenly became crystalline; the highly deliquescent product was washed with acetone-ether and dried over calcium chloride (yield 43 per cent.) (Found: Co = 16.0; NH₃ = 18.2; Cl = 19.0; H₂O at 100° = 9.7. The dihydrate requires Co = 15.9; NH₃ = 18.3; Cl = 19.1; 2H₂O = 9.7 per cent.). This *hydrogen dichloride* consisted of bright red, rhomboidal plates deliquescent in air to a red liquid which then solidified to a mass of the purplish-red plates of the normal chloride. The normal salt was also obtained by adding pyridine to the concentrated, bright red, strongly acid, aqueous solution of the hydrogen dichloride. This red aqueous solution was rendered purple by alkali and also by progressive dilution, the normal chloride separating in characteristic purplish-red, flattened needles. The hydrogen dichloride dissolved in alcohol and was reprecipitated therefrom by acetone or ether.

Salicylatotetramminocobaltic Hydrogen Dibromide,

—To the blood-red solution of 10.8 grams of the normal bromide in 7 c.c. of water and 4.5 c.c. of 60 per cent. hydrobromic acid (\equiv 2.7 grams HBr) were added equal volumes of acetone and ether, when bright red plates separated, which were washed with ether (yield = 78 per cent.) (Found: Co = 13.2; NH_3 = 15.3; Br = 35.8; H_2O at 75° = 4.2. The monohydrate requires Co = 13.4; NH_3 = 15.4; Br = 36.2; H_2O = 4.1 per cent.).

The *hydrogen dibromide* separated in dark red, rhomboidal plates bright red by transmitted light. It dissolved very readily in water to a blood red, strongly acid solution from which hydrogen bromide in ether slowly deposited the unchanged dibromide, whereas pyridine precipitated the normal bromide in purple-red, six-sided plates.

Salicylatotetramminocobaltic Hydrogen Mercurihalides,

—These three complex salts were found to be anhydrous.

(i) *Hydrogen mercurichloride* was formed as a brownish-red paste which rapidly darkened and became crystalline on adding 4 grams of mercuric chloride, dissolved in 3 c.c. of 10N-hydrochloric acid, to 5.6 grams of the hydrogen dichloride in 5 c.c. of water and 20 c.c. of 2N-hydrochloric acid. The product was recrystallised from hot N-hydrochloric acid, when dark red, rhomboidal plates crystallised out on cooling (yield 75 per cent.) (Found: Co = 9.7; NH_3 = 11.2; Hg = 32.8. The anhydrous hydrogen mercurichloride requires Co = 9.7; NH_3 = 11.2; Hg = 33.1 per cent.). This complex salt was moderately soluble in water to a red, strongly acid solution.

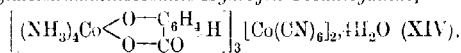
(ii) *Hydrogen Mercuribromide*.—On triturating 3.6 grams of mercuric bromide with 3.61 grams of the cobaltamine bromide and 20 c.c. of warm N-hydrobromic acid the mercuric bromide dissolved and a dark red, crystalline powder then separated. This product was recrystallised in brownish-red, six-sided plates from hot N-hydrobromic acid and washed with ether (yield 72 per cent.) (Found: Co = 7.6; NH_3 = 8.8; Hg = 25.4. The anhydrous hydrogen mercuribromide requires Co = 7.5; NH_3 = 8.7; Hg = 25.6 per cent.). This complex salt was sparingly soluble in water (1 in 50) to a strongly acid solution turned purple by alkalis.

(iii) *Hydrogen Mercuriodide*.—Cobaltamine bicarbonate (1.95 grams) was dissolved in 3 c.c. of colourless 4N-hydriodic acid and the deep red solution added to 2.72 grams of mercuric iodide in 3 c.c. of the hydriodic acid. The mercuric iodide dissolved and a chocolate-brown, crystalline powder separated; the latter, when

recrystallised from hot *N*-hydriodic acid, furnished brilliant purple, black, six-sided plates brownish-red by transmitted light (yield 84 per cent.) (Found: Co = 6·2; NH₃ = 6·9; Hg = 20·6. The anhydrous hydrogen mercuri-iodide requires Co = 6·1; NH₃ = 7·0; Hg = 20·6 per cent.).

This salt is only very sparingly soluble in water (1 in 100) to a strongly acid, red solution. The acidic red solutions of the three mercurihalides are rendered purple by alkalis and yield white precipitates with sodium hydroxide or 5*N*-ammonia.

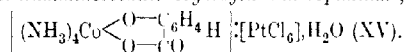
Salicylatotetramminocobaltic Hydrogen Cobalticyanide,



—The cobaltammine bicarbonate (4·61 grams) dissolved to a red solution in 16·8 c.c. of 1·8*N*-cobalticyanic acid (\equiv 2·18 grams H₃CoCy₃) and after three weeks the dark red needles which had separated were recrystallised from 3 c.c. of cobalticyanic acid and 5 c.c. of hot water, when a yield of 71 per cent. was obtained (Found: Co = 22·6; NH₃ = 15·6; H₂O at 97° = 5·8. The tetrahydrate requires Co = 22·8; NH₃ = 15·8; 4H₂O = 5·6 per cent.).

The hydrogen cobalticyanide consisting of glistening, rose-pink, rhomboidal plates dissolved readily in water to a red, strongly acid solution.

Salicylatotetramminocobaltic Hydrogen Chloroplatinate,



—A brown, crystalline precipitate (yield 73 per cent.) separated on dissolving 0·324 gram of cobaltammine bicarbonate in 20 c.c. of *M*/20-chloroplatinic acid (\equiv 0·195 gram Pt), the supernatant liquid becoming almost colourless (Found: Co = 8·6; Pt = 28·3; H₂O at 97° = 2·5. The hydrated hydrogen chloroplatinate requires Co = 8·6; Pt = 28·3; H₂O = 2·6 per cent.).

The brownish-red, glistening, square tablets of this hydrogen salt, which were yellow by transmitted light, were almost insoluble in cold water, dissolving somewhat more readily in hot 2*N*-hydrochloric acid to a bluish-red solution and separating on cooling in brown crystals. This salt did not evolve hydrogen chloride with cold concentrated sulphuric acid.

The authors desire to express their thanks to the Advisory Council of the Department of Scientific and Industrial Research for grants which have helped to defray the expense of this investigation.

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EDGBASTON.

[Received, April 19th, 1925.]

CCXIV.—*Studies on Thallium Compounds. Part II.*
The Reduction of Thallie Compounds with Ferrous
Sulphate and with Sodium Arsenite.

By ARTHUR JOHN BERRY.

In a previous paper (I., 1922, 121, 394), it was shown that thallie compounds could be reduced quantitatively with ferrous sulphate and with sodium arsenite. It was pointed out (*loc. cit.*, p. 399) that volumetric methods of analysis founded on these two reactions yielded results in essential agreement among themselves, but appreciably lower than those obtained by the gravimetric method of weighing as thalious iodide. It was considered desirable to investigate these reactions more fully, and the results obtained are summarised in the present communication.

Velocity of the Reaction $\text{Tl}_2(\text{SO}_4)_3 + 4\text{FeSO}_4 = \text{Tl}_2\text{SO}_4 + 2\text{Fe}_2(\text{SO}_4)_3$.

The velocity experiments were carried out at 0° in the following manner. The measured quantities of ferrous sulphate and thallie sulphate solutions, both containing much free sulphuric acid, having been cooled to 0°, were mixed in a beaker immersed in a large vessel containing ice and water. The contents of the beaker, and also the ice and water, were stirred mechanically. In every experiment, the ferrous and thallie salts were taken in equivalent proportions, but the actual concentrations were varied in separate experiments. Definite volumes of the solution were withdrawn at regular intervals of time into flasks containing a little crushed ice, and immediately titrated with potassium dichromate.

A number of experiments were performed of which three are selected for comparison. The volume of the reaction mixture was in every case 500 c.c., but the concentrations varied from *N*/140 to *N*/35. The volume of liquid withdrawn for titration was either 50, 70, or 100 c.c., depending on the concentration. The solution of potassium dichromate was of *N*/20 strength: *v* = volume of it required to titrate the 500 c.c.

1. Concentration <i>N</i> /140.		2. Concentration <i>N</i> /70.		3. Concentration <i>N</i> /35.	
Time (mins.).	<i>v</i> .	Time (mins.).	<i>v</i> .	Time (mins.).	<i>v</i> .
0	70*	0	140*	0	280*
10	56	10	100	15	175
30	45	30	79.5	35	129
50	42.5	50	72	55	107
70	37.5	70	67	75	91
90	35	90	61	95	77
				120	69
				150	60

* Calculated quantities.

If velocity coefficients are calculated from these figures, the results will indicate a reaction of the second order. The coefficients are, however, somewhat irregular, particularly in the experiments at the lower concentrations. On the other hand, if we determine the order of the reaction from the time required for half of the original mixture to undergo transformation according to the equation

$$n = 1 + \log \frac{t_1}{t_2} / \log \frac{c_2}{c_1}$$

(van't Hoff, "Studies in Chemical Dynamics," translated by Ewan, p. 103), where n is the order of the reaction, c_1 and c_2 are the different initial concentrations, and t_1 and t_2 are the corresponding times required for half of the original mixture to undergo transformation, we shall obtain the following results:

$$\text{from (1) and (2), } n = 1 + \log \frac{90}{35} / \log 2 = 1.71;$$

$$\text{from (2) and (3), } n = 1 + \log \frac{55}{25} / \log 2 = 2.14;$$

$$\text{from (1) and (3), } n = 1 + \log \frac{90}{25} / \log 4 = 1.93;$$

which shows clearly that the reaction is of the second order.

This reaction is evidently similar to the reduction of ferric chloride by stannous chloride investigated by Noyes (*Z. physikal. Chem.*, 1895, **16**, 546), who found that the latter reaction was of the second order in presence of sufficient hydrochloric acid, although it was of the third order when the solution was as free from acid as possible.

When the residual liquid from a velocity experiment was heated to boiling and cooled, it was found that the reaction had proceeded to completion. It is obvious, therefore, that if, as in analytical work, excess of ferrous sulphate is used, the method should be capable of giving a true measure of the amount of thallous salt in solution.

The Sodium Arsenite Method. The method of analysis with sodium arsenite described in the previous paper (*loc. cit.*, p. 398) was modified to obviate the necessity of removing the reduced thallium as iodide before estimating the excess of sodium arsenite. In the experiments to be described, the excess of sodium arsenite was titrated with a solution of sodium hypochlorite. It was found that a solution of sodium hypochlorite could be standardised by titrating a hot solution of sodium arsenite containing a little thallous sulphate, the end-point observed being the appearance of a brown colour due to incipient precipitation of thallous oxide at the moment when the arsenic solution was completely oxidised. The results

obtained in this manner were identical with those obtained by titrating the sodium arsenite in the cold, and determining the end-point in the usual manner with starch-potassium iodide paper. Thallous oxide, dried at the ordinary temperature by exposure over concentrated sulphuric acid in a vacuum desiccator, can be dissolved in sodium arsenite solution of about $N/10$ -strength after heating for some time, complete reduction taking place. The excess of sodium arsenite is then estimated by titration with sodium hypochlorite.

The probable error of experiment in volumetric estimations by these two methods would be of the order of one-half of 1 per cent., and in any case would not exceed 1 per cent. The cause of the low results is therefore to be sought in the thallous oxide, and accordingly various methods of preparation were examined.

Analyses of Thallous Oxide Prepared by Various Methods.—(1) *Oxidation of thallous sulphate by potassium ferricyanide in alkaline solution.* This method has been described in the previous paper.

Gram of Tl_2O_3 taken	0.312	0.357	0.217	0.5575
Gram of Tl_2O_3 found	0.306	0.3505	0.213	0.548
Method	$FeSO_4$	As_2O_3	As_2O_3	As_2O_3

The percentage of thallium from these experiments is 87.9. The calculated value for Tl_2O_3 is 89.5 per cent.

(2) *Hydrolysis of thallous sulphate.* The very great extent to which solutions of thallous sulphate are hydrolysed suggested the possibility of purifying the oxide by dissolving it in dilute sulphuric acid, and diluting the resulting solution largely with water to reprecipitate the oxide. These experiments were carried out in the following manner.

Two hundred and fifty c.c. of a 1 per cent. solution of thallous oxide in dilute sulphuric acid were thoroughly shaken with ten times the volume of water. The oxide was precipitated as a brown powder. The bulk of the clear liquid was then removed with the aid of a syphon, and the precipitate thoroughly washed till every trace of sulphuric acid was removed. The wet oxide was then removed, without filtering, into a dish, and dried by exposure over concentrated sulphuric acid in a vacuum desiccator.

Gram of Tl_2O_3 taken ...	0.311	0.313	0.308	0.408	0.3115	0.3385
Gram of Tl_2O_3 found ...	0.299	0.302	0.298	0.389	0.300	0.323
Method	$FeSO_4$	$FeSO_4$	As_2O_3	As_2O_3	As_2O_3	As_2O_3

From these values the percentage of thallium is found to be 85.9.

(3) *Oxidation of thallous chloride to thallous chloride and precipitation of the oxide.* Thallous chloride was suspended in water, and saturated with washed chlorine until a clear solution of thallous

chloride was obtained. Excess of sodium carbonate solution was added to precipitate the thallic oxide, which was then carefully washed and dried as usual.

Gram of Tl_2O_3 taken	0.4015	0.3665	0.3765	0.4195
Gram of Tl_2O_3 found	0.391	0.357	0.371	0.412
Method	$FeSO_4$	$FeSO_4$	As_2O_3	As_2O_3

The percentage of thallium is thus found to be 87.6.

(4) *Oxidation of thallous sulphate by hydrogen peroxide in alkaline solution.* Thallium was dissolved in sulphuric acid, and the solution after dilution with water saturated with hydrogen sulphide. The object of this treatment was to remove traces of lead. A very insignificant precipitate was obtained, which as regards appearance indicated a trace of selenium. This precipitate was removed, and the resulting solution evaporated to small bulk to remove most of the free sulphuric acid. Thallic oxide was then precipitated by adding excess of sodium hydroxide and hydrogen peroxide as described by Rabe (*Z. anorg. Chem.*, 1906, **48**, 427), and after thorough washing, dried as in the other experiments.

Gram of Tl_2O_3 taken	0.307	0.296
Gram of Tl_2O_3 found	0.290	0.279
Method	As_2O_3	As_2O_3

The percentage of thallium is thus 84.4.

Further experiments were made in which thallium was converted into thallous sulphate, and freed from traces of lead and selenium by hydrogen sulphide as already described, and then converted into thallic oxide by oxidation with alkaline potassium ferrieyanide, but low results were again obtained when the oxide was analysed by these volumetric methods. Whatever method of preparation was employed, the percentage of thallium, as determined by measurement of the available oxygen, was always lower than the calculated value, the difference varying from 2 to 6 per cent.

To what cause is the deficit due? The results would be readily intelligible if the thallic oxide preparations contain small quantities of thallous impurity. Experiments were therefore made to test the various preparations for small quantities of thallous material; and it was found that all the preparations, when dissolved in hydrochloric acid,* reacted with dilute potassium permanganate (N/100), the amount of permanganate required corresponding approximately to the deficit of thallic oxide observed.

(a) *Thallic oxide prepared from the chloride* (found 87.6 per cent. Tl). 0.4905 Gram of Tl_2O_3 , dissolved in hydrochloric acid, required 5 c.c. of N/100- $KMnO_4$.

* These solutions were slightly turbid in consequence of the presence of the small quantity of thallous chloride.

(b) *Thallic oxide prepared by Rabe's method* (found 84.4 per cent. Tl). 1.498 Gram of Tl_2O_3 , dissolved in hydrochloric acid, required 14 c.c. of $N/100\text{-KMnO}_4$.

The difference between the estimated and the calculated percentage of thallium (89.5) is 1.9 in the former case and 5.1 in the latter, and the permanganate titrations for similar weights of oxide are approximately in the same ratio. The experiments were performed under similar conditions as regards quantity and concentration of acid, and blank experiments were made to determine the volume of permanganate decolorised by the hydrochloric acid in the absence of the thallic oxide. In view of the uncertainties connected with determinations with potassium permanganate in presence of hydrochloric acid, exact agreement is not to be expected; but it seems legitimate to conclude from these experiments that thallic oxide prepared in various ways contains small quantities of thallous material, the amount varying with the conditions of precipitation. The thallous compound is evidently adsorbed or held in solid solution, and cannot be removed by washing.

Solutions of thallic sulphate containing free sulphuric acid are remarkably stable, no loss of available oxygen, as determined by these volumetric methods, being observable over long periods. One example may suffice. A solution containing 9.86 grams of Tl_2O_3 per litre as determined by ferrous sulphate and potassium dichromate, or 10.1 grams of Tl_2O_3 as determined gravimetrically as thallous iodide, was found to be unaltered in strength as determined by measurement of the available oxygen eight months later. When this solution was titrated with $N/100$ -potassium permanganate in presence of hydrochloric acid, and the result taken in conjunction with the determination with ferrous sulphate and potassium dichromate, the total thallium calculated as Tl_2O_3 was found to be 0.2 grams per litre.

Rabe, who has devoted much attention to the brown and black modifications of thallic oxide, has found (*Z. anorg. Chem.*, 1907, 35, 130) that when dried in a vacuum desiccator containing phosphoric oxide, both varieties still contain very small quantities of water. The quantity of water was found to be of the order of 0.7 per cent. in the case of the brown oxide, and 0.2 per cent. in the case of the black oxide. Rabe has claimed (*loc. cit.*), but solely on the evidence of gravimetric analysis, that no loss of oxygen takes place when either variety is heated at 500°, and that it is necessary to heat thallic oxide to this temperature to obtain it in perfectly anhydrous condition. When the brown oxide is heated, it is changed into the black variety.

The author has determined the available oxygen in thallic oxide

previously heated at 500°. The ferrous sulphate method alone was used, because after heating to this temperature the oxide dissolves in sodium arsenite with such extreme slowness as to render that method impracticable. The heating of both specimens of oxide was carried out in a platinum boat, placed inside a silica tube in a horizontal electric furnace.

The following results were obtained :

	Thallic oxide (black) prepared by oxidation with alkaline potassium ferriyanide.		Thallic oxide (brown) prepared by hydroly- sis of the sulphate.	
Gram of Tl_2O_3 taken	0.321	0.2025	0.4255	0.4285
Gram of Tl_2O_3 found	0.316	0.198	0.399	0.419
Percentage of thallium.....	85.9		83.8	

The black oxide is therefore quite stable at 500°. On the other hand, the brown oxide prepared by hydrolysis of the sulphate has suffered an appreciable loss of oxygen, the percentage of thallium as measured by the available oxygen falling from 85.9 to 83.8 per cent. This result was not unexpected in view of the greater reactivity of the brown oxide. Whether these varieties are truly polymorphic or differ merely as regards degree of aggregation is at present unknown.

The author desires to renew his cordial thanks to Sir William Pope and Mr. Heycock for their unfailing interest in this investigation.

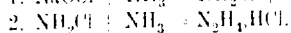
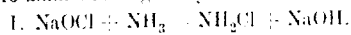
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CXXV.—*Preparation of Hydrazine by Raschig's Method.*

By REGINALD ARTHUR JOYNER.

HYDRAZINE was first prepared by Curtius and Jay in 1889, but it was not until the method of preparing it from sodium hypochlorite and ammonia was devised by Raschig (*Ber.*, 1907, 40, 4588) that the technical manufacture could be attempted.

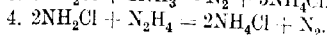
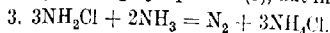
Raschig found that in the interaction of ammonia and sodium hypochlorite chloroamine is formed quantitatively, which reacts with more ammonia to give hydrazine :



Hydrazine hydrate is, of course, formed in presence of the caustic soda.

Raschig found that the second reaction only takes place to any considerable extent when a very large amount of ammonia is present, and also glue or some such substance, when a yield up to 60 or 70 per cent. may be obtained.

Another reaction which takes place, giving rise to nitrogen, is represented by Raschig by equation (3), but in view of the reducing



properties of hydrazine, it more probably occurs in accordance with equation (4).

The following experiments were made to ascertain the effect on the yield of hydrazine of varying the concentrations of ammonia, sodium hypochlorite, and glue, and of replacing the last by other substances. The concentration of hydrazine throughout was determined by titrating the solution with *N*/10-iodine solution in presence of sodium bicarbonate, $\text{N}_2\text{H}_4 + 4\text{I} = \text{N}_2 + 4\text{HI}$, the ammonia having been approximately neutralised with acid.

EXPERIMENTAL.

Connexion between the Yield of Hydrazine and the Molecular Ratio of Ammonia to Sodium Hypochlorite.

Mixtures of 10 c.c. of 3.95*N*-sodium hypochlorite, 1 c.c. of a 10 per cent. solution of glue, and varying volumes of 7.95*N*-ammonia were diluted with water to 100 c.c., heated at 80–90°, cooled, and the quantity of hydrazine estimated. The results are given in Table I, where *a* = percentage yield of hydrazine calculated on the quantity of sodium hypochlorite, and *b* = molecular ratio of ammonia to sodium hypochlorite.

TABLE I.

The solution contained 0.10 gram of glue and 0.0197 mol. of sodium hypochlorite in 100 c.c. of the mixture.

Mols. of NH_3 .	<i>a</i> .	<i>b</i> .	$(\log b - 0.200). a$.
0.0397	5.7	2.62	(1.85)
0.0536	11.0	2.83	2.29
0.0705	18	4.04	2.26
0.1103	26	6.06	2.23
0.1590	32	8.08	2.21
0.1989	37.5	10.1	2.13
0.2975	52	20.2	2.13
0.7155	63	56.4	2.16
1.510 *	75	76.8	2.25

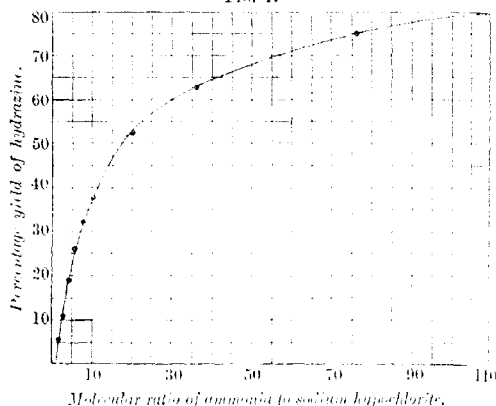
* In this experiment the volume was made up to 200 c.c. using 2 c.c. of the glue solution.

The results are given in Fig. 1. The graph approximates to logarithmic curve and the expression $(\log b - 0.200). a$ is constant or values of *b* between 2.8 and 77.

Effect of the Concentration of the Gelatin on the Yield of Hydrazine.

For these experiments it was found necessary to use very pure ammonia solution in order to obtain consistent results; some ammonias, without any gelatin, gave yields up to 10 or 15 per cent. of hydrazine, whilst others gave only 1 to 2 per cent.

FIG. 1.



In carrying out these experiments, fixed amounts of ammonia and of sodium hypochlorite were heated with varying amounts of gelatin and the yield of hydrazine was estimated. The results are given in Tables II, III, and IV, and graphically in Fig. 2.

TABLE II.

0.400 Mol. of NH_3 and
0.0100 mol. of NaOCl
in 110 c.c. of the
solution.

Mg. of gelatin added.	Percentage yield of hydrazine.
0	2.0
1.9	8.8
2.9	18.2
3.9	25.4
4.9	30.8
10.9	39.0
30.9	48.3
100.9	51.0
100.9	51.0

TABLE III.

0.080 Mol. of NH_3 and
0.0200 mol. of NaOCl
in 110 c.c. of the
solution.

Mg. of gelatin added.	Percentage yield of hydrazine.
0	1.6
1.9	3.95
3.9	10
5.9	13.2
10.9	15.1
50.9	17.0
100.9	17.5

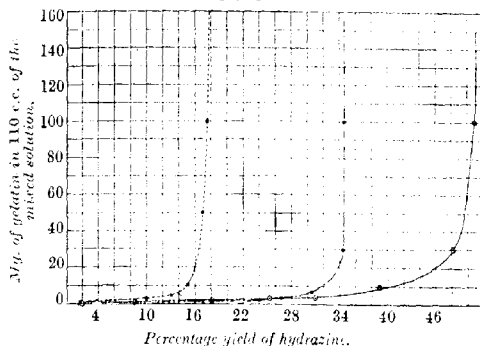
TABLE IV.

0.400 Mol. of NH_3
and 0.050 mol. of
 NaOCl in 110 c.c. of
the solution.

Mg. of gelatin added.	Percentage yield of hydrazine
0	3.05
0.59	9.9
1.9	16.9
2.9	24
4.9	26.6
7.9	30.5
30.9	31.4

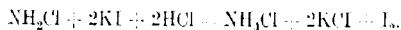
It is evident from the curves that the yield of hydrazine is almost directly proportional to the concentration of the gelatin at low concentrations, but the relative activity of the latter rapidly diminishes with increasing concentration. The reaction is very sensitive to small amounts of gelatin, and it is probable that 1×10^{-5} gram of gelatin or similar substance could be detected in a volume of 10 c.c.

FIG. 2.



The Partition of Chloroamine between Ether and Various Aqueous Solutions.

One of the possible explanations of the action of glue is that it forms an additive compound with chloroamine which reacts with ammonia to give hydrazine. In order to find whether any such compound was formed in considerable amount, experiments were carried out on the partition of chloroamine between ether and various aqueous solutions. A solution of chloroamine made by adding ammonia to sodium hypochlorite was extracted with ether, the ethereal extract being kept in ice. This precaution was unnecessary, as it was found that ether-chloroamine solutions were very stable. The chloroamine in the ether or in the water was readily estimated by means of the iodine it liberated from acidified potassium iodide solution:



The partition experiments were carried out at the temperature stated by adding the stock ether solution to the various aqueous solutions and thoroughly shaking the mixtures. After the two phases had separated, the concentration of the chloroamine was determined in both. The results are given in Tables V and VI.

TABLE V.

Partition of chloroamine between water and ether, and between glue solution and ether at 0°.

C.c. of N/10-iodine required for 2 c.c. of each solution.

Ether.	Water.	Ratio.	Ether.	Glue solution.	Ratio.
3.1	2.2	1.4	3.2	2.1	1.5
3.1	2.2	1.4	3.2	2.1	1.5

TABLE VI.

Partition of chloroamine between 2N-aqueous ammonia and ether, between water and ether, and between ether and an aqueous solution of glue-ammonia at - 8°.

C.c. of N/10-iodine required for 2 c.c. of each solution.

2N-Am-			Ammonia			Ammonia-glue		
Ether.	Water.	Ratio.	Ether.	monia.	Ratio.	Ether.	glue.	Ratio.
5.8	4.5	1.29	5.7	4.5	1.27	5.6	4.0	1.40
5.9	4.5	1.32	5.7	4.2	1.35	5.7	4.0	1.42

The above results show, if anything, that in the presence of glue the chloroamine tended to pass into the ether phase. Had there been any combination between the glue and the chloroamine, the concentration of the latter in the aqueous phase would have increased. The same result was obtained when the aqueous phase contained ammonia and also ammonia and glue, and therefore it is unlikely that an intermediate compound is formed between chloroamine and glue, or chloroamine and ammonia, or chloroamine, glue, and ammonia.

Influence of Various Salts on the Formation of Hydrazine.

Preliminary experiments having shown that the presence of ammonium salts tended to reduce the yield of hydrazine, a series of experiments was carried out to ascertain the effect produced by various salts on reacting mixtures of ammonia, glue, and sodium hypochlorite. The results are given in Tables VII and VIII.

TABLE VII.

Effect of various salts on the yield of hydrazine obtained from 12 mols. of ammonia, 1.5 grams of glue, 0.4 mol. of sodium hypochlorite, and 0.2 mol. of sodium hydroxide in 1280 c.c. of solution.

Salt added.	Weight (grams).	% Hydrazine formed.	Salt added.	Weight (grams).	% Hydrazine formed.
No salt	—	52	NH ₄ Cl	10	1.2
(NH ₄) ₂ SO ₄	44	6	"	7.5	52
KCl	51	56	"	15	41
No glue	—	0.1			

TABLE VIII.

Effect of varying amounts of ammonium chloride and other substances in the formation of hydrazine from a mixture of 5.1 mols. of ammonia, 0.75 gram of glue, 0.15 mol. of sodium hypochlorite, and 0.090 mol. of sodium hydroxide in 500 c.c. of water.

Substance added.	Weight (grams).	% Hydrazine formed.	Substance added.	Weight (grams).	% Hydrazine formed.
None	—	50	NH ₄ Cl	16	4.1
"	—	54	NH ₄ XO ₃	12	35
NH ₄ Cl	2	55	(NH ₄) ₂ SO ₄	19	33
"	4	53	Na ₂ SO ₄	10.7	54
"	8	34	NaOH	6.0	52
"	12	6.3	NH ₄ HCO ₃	12.0	4.5

These experiments show that the presence of ammonium-ion lowers the yield of hydrazine to a great extent. This effect was noticeable when the quantity of ammonium salt added was sufficient to react with the free sodium hydroxide originally present and also with that set free during reaction 1 (p. 1114). In cases such as this the hydrazine hydrochloride will give ammonium chloride and hydrazine hydrate, as the latter is a weaker base than an equivalent solution of ammonia in water, and therefore reaction 2 (p. 1114) will take place in the presence of increasing concentrations of ammonium-ion.

Gelatin in solution has slightly acid properties (Wintger and Vogel, *Kolloid Z.*, 1922, **30**, 45; Lloyd and Mayes, *Proc. Roy. Soc.*, 1922, [B], **93**, 69), and in the presence of ammonia a certain amount of ammonium-ion is necessarily formed. It was found that when the sodium hypochlorite was nearly neutral an increase in the yield of hydrazine was brought about by the addition of about 0.01 mol. of sodium hydroxide per litre.

When hypochlorous acid (pure) and chloroamine were used instead of an equivalent quantity of sodium hypochlorite, about 12 per cent. of hydrazine was formed instead of 60 per cent., whilst when calcium hypochlorite was used the yield was about 25 per cent. In the case of the first two substances there would be practically no free hydroxyl-ion, and in the case of the last the relative concentration is small, owing to the insolubility of the calcium hydroxide set free.

Effect of the Addition of Hydrazine on the Yield of Hydrazine obtained from a Mixture of Sodium Hypochlorite, Glue, and Ammonia.

A known quantity of hydrazine hydrate solution was added to a mixture of ammonia, glue, and sodium hypochlorite and the total amount of hydrazine was estimated after the reaction had

taken place. It will be seen from results given in Table IX that when the hydrazine was added before the sodium hypochlorite the yield was less than that obtained when the two substances were added in the reverse order. Evidently the hydrazine brings about a decreased yield, but the decrease is not proportional to the amount of hydrazine added.

TABLE IX.

Showing the effect on the yield of hydrazine of adding hydrazine to a mixture of ammonia and bleach.

C.c. of N_2H_4 added.	Equivalent in c.c. of $N/10$ -iodine.	Total titration at the end.	Loss due to N_2H_4 added.	Loss per c.c. added.	Yield per cent. on bleach added.	Remarks.
0	0	38.7	0		79	
0	0	39.4	0		80	
0	0	39.1	0		80	
2	14.7	48.7	5.1	2.6	69	N_2H_4 added before NaOCl.
2	14.7	50.3	3.4	1.7	73	N_2H_4 added after NaOCl.
1	7.35	44.7	1.8	1.8	76	
5	36.7	68.1	7.7	1.5	64	
17	124.9	143.1	20.0	1.2	35	
5	36.7	69.2	6.6	1.3	66	Large excess of glue.

Substitution of Other Substances for Gelatin as Catalyst.

The substances employed may be divided into those giving apparently homogeneous mixtures with water and those giving heterogeneous mixtures. Of the former, urea, saccharin, sodium azide, sodium oleate, sodium palmitate, and lithium chloride had no catalytic effect.

Gelatin, glue, and peptone produced the same effect at all the concentrations employed. Starch, dextrin, and sucrose catalysed the reaction, but only appreciably when used in amounts 100 to 300 times that of the gelatin. The effect of the sodium salts of glutamic acid, tyrosine, tryptophan, and uric acid was insignificant. Peptised silicic and stannic acids had strong catalysing actions, the yield of hydrazine obtained with stannic acid being about equal to that produced by one-third the quantity of gelatin; with silicic acid, however, a yield equal to that obtained with glue could not be attained.

It was found that the reaction could be catalysed by substances such as animal charcoal, wood charcoal, asbestos powder, and powdered meerschaum, when these were present in relatively large quantities. Kieselguhr, calcium phosphate, silica gel, French chalk, and kaolin had no action.

Some of the substances were ground in a Plauson colloid mill, and it was found that by this means the maximum yield could be attained with a smaller quantity of substance.

It has been stated that there is no difference in the catalysing properties of gelatin, glue, and peptone, and that the amino-acids have comparatively little catalysing action. As peptone is produced from gelatin by hydrolysis, on boiling the latter with hydrochloric acid a stage should come at which the catalysing action of the product will have diminished. It was found that on boiling a 10 per cent. solution of gelatin in 5*N*-hydrochloric acid the activity of the product decreased after ten minutes and after sixty minutes was only about 15 per cent. of that of the original solution. By this means it was found possible to produce a catalyst of low viscosity which did not froth on boiling, but which possessed a catalysing action equal to that of gelatin.

Mechanism of the Formation of Hydrazine.

It is improbable that the action of the gelatin is due to the formation of intermediate compounds with chloroamine, because it was shown in the partition experiments that the existence of any such compound is not likely. Moreover, this explanation does not account for the behaviour of the substances which form heterogeneous mixtures with water. The fact that the addition of hydrazine to the reacting mixture of glue, ammonia, and sodium hypochlorite (p. 1120) causes a decrease in the yield indicates that the by-reaction takes place according to equation 4 (p. 1115). The catalyst therefore accelerates reaction 2 or retards reaction 4. The former effect would be produced by strong absorption of the ammonia by the particles of glue. This explanation of the action of the catalyst is in harmony with the behaviour of insoluble substances such as the charcoals, which are known to adsorb ammonia to a large extent. It is interesting to note that gelatin peptones, which are the most active catalysts in the Raschig reaction, are also active in the inhibition of the breakdown of hydrogen peroxide by platinum (Fredale, T., 1921, **119**, 109) and also in the inhibition of the decomposition of hydroxylamine by colloidal platinum (Findlay and Thomas, *ibid.*, p. 170).

This work was carried out at Ardeer Factory, Stevenston, and the author wishes to thank Mr. Rintoul, O.B.E., F.I.C., and Messrs. Nobel Industries, Ltd., for permission to publish this paper.

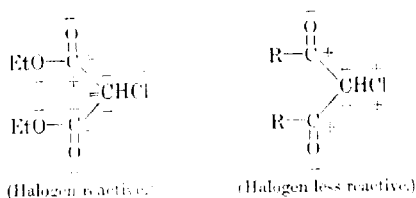
ARDEER FACTORY, STEVENSTON.

[Received, January 17th, 1923.]

CXXVI.—*The Labile Nature of the Halogen Atom in Organic Compounds. Part VIII. The Action of Hydrazine on the Halogen Derivatives of Acetoacetic and Benzoylacetic Esters and of Benzoylacetone.*

By ALEXANDER KILLEN MACBETH.

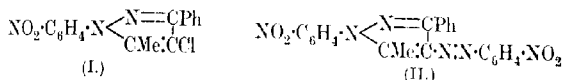
IN a previous paper of this series attention was directed to the fact that mono- and di-chloromalonic esters have a greater oxidising action on hydrazine than the 3-chloro-derivatives of acetylacetone (T., 1922, 121, 1116). This observation was further supported by the study of a series of substituted chloromalonic esters (*ibid.*, p. 2169), and it was found that substances of this type are quantitatively reduced by hydrazine hydrate with liberation of nitrogen. The different chloro-diketones examined ($\gamma\gamma$ -dichloroacetylacetone, 4 : 4-dichloro-1 : 1-dimethylcyclohexane-3 : 5-dione, cyclohexane-*spiro*-4 : 4-dichlorocyclohexane-3 : 5-dione, and the corresponding monochloro-compounds) were found to be unacted upon by hydrazine hydrate at the ordinary temperature, and it was suggested that the greater reactivity of the chlorine atom in the malonic derivatives was connected with the fact that it was subjected to the influence of the two ethoxyl groups in addition to that of the two keto-groups. On the polarity basis this is represented as follows :



Gupta and Thorpe (T., 1922, 121, 1896) take exception to this view, because if it is applied to the case of the bromo-compounds, dibromomalonic ester should brominate more readily than 4 : 4-dibromo-1 : 1-dimethylcyclohexane-3 : 5-dione; and this they find is contrary to the experimental facts. It is well known that in general the introduction of a carbethoxyl group for the carbonyl group in the diketones results in decreased reactivity; and it was on account of the exceptional behaviour of the chloromalonic esters in the reactions referred to that we directed attention to the supposed influence of the additional ethoxyl groups. The chlorine atom certainly seems to be susceptible to such influence, for we have examined further cases in support of our previous observations and

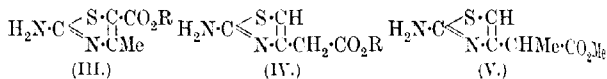
found that, whereas the chloro-derivatives of diketones are not reduced by hydrazine, the halogen compounds in which an additional ethoxyl group is present are readily acted upon by this reagent. Thus, γ -chloro- and $\gamma\gamma$ -dichloro-benzoylacetone liberate no nitrogen from hydrazine hydrate at the ordinary temperature, but the halogen derivatives of acetoacetic and benzoyl-acetic esters liberate nitrogen quantitatively under the same conditions. From these results it would appear that the reactivity of the chlorine atom is increased by the introduction of the ethoxyl group, and this may be explained on the polarity basis in the usual way.

γ -Chloro- and $\gamma\gamma$ -dichloro-benzoylacetone are conveniently prepared by the action of sulphuryl chloride on the parent diketone. They are readily converted into substituted pyrazoles by the action of *p*-nitrophenylhydrazine. Thus γ -chlorobenzoylacetone gives rise to 4-chloro-3(or 5)-phenyl-1-*p*-nitrophenyl-5(or 3)-methylpyrazole (compare Morgan, Drew, and Barker, T., 1922, 121, 2457), whilst the dichloro-compound is converted into 4-*p*-nitrobenzeneazo-3(or 5)-phenyl-1-*p*-nitrophenyl-5(or 3)-methylpyrazole (II) :



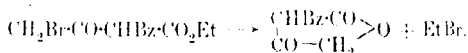
From the results obtained it would appear that hydrazine may be employed to determine the position of the halogen atom in compounds of the acetoacetic series. It is well known that bromo-compounds of this class of ester in which the halogen atom is attached to the α -carbon atom readily change into the corresponding α -bromo-compound, especially in the presence of hydrobromic acid (Hantzsch, *Ber.*, 1894, 27, 356, 3168; Conrad, *Ber.*, 1896, 29, 1042). Since the γ -bromo-esters are unacted upon, whilst the α -compounds are quantitatively reduced by hydrazine hydrate, this reagent may be conveniently employed to determine the amount of the α -form present, and so to follow the α to γ change. The identification of the two forms has hitherto been based on the formation of thiazole derivatives by the action of thiourea (Hantzsch, *Ber.*, 1892, 25, 728; *Annalen*, 1894, 278, 61), the α -compound giving an ester of amino- α -ethylthiazolecarboxylic acid (III), and the γ -compound an ester of aminothiazolylacetic acid (IV). The substituted esters also give rise to derivatives of a similar type, methyl γ -bromoethyl-acetoacetate, for example, being converted into methyl amino-thiazolylpropionate (V) (Conrad and Kreichgauer, *Ber.*, 1896, 29, 046). It is evident that although the isolation of compounds of the thiazole type gives an indication of the nature of the main constituent of a bromoacetoacetic ester, it cannot be employed as

the basis of an accurate estimation of the amounts of the α - and γ -forms present in a mixture of the bromo-compounds. The hydrazine reaction is found to be very convenient in such work in the case of the substituted halogen esters.



The ease with which the α -bromoacetoacetic esters pass over into the corresponding γ -compounds in the presence of hydrobromic acid makes it a matter of difficulty to prepare the pure α -derivative by ordinary bromination methods. Brühl (*Ber.*, 1903, **36**, 1731) pointed out that if the bromination is carried out in the presence of a solution of sodium hydroxide the pure α -derivative will be obtained; and this is found to be the best method of preparing ethyl α -bromoacetoacetate. Smith (*J. Amer. Chem. Soc.*, 1922, **44**, 216) has shown that if the ester is brominated by introducing the bromine vapour by a rapid current of air—which also sweeps out the hydrogen bromide formed—the product will consist mainly of the α -bromo-derivative. This method of bromination is found to be very convenient in the preparation of the substituted α -bromo-esters, which are thus obtained free from the γ -derivative.

In brominations by this method it is essential that the operation, and the subsequent purification, be carried out without delay, as otherwise migration of the halogen atom from the α - to the γ -position will take place. This was specially noted in the case of ethyl bromobenzylacetoacetate, which decomposed with the evolution of much vapour (probably ethyl bromide) on distillation under reduced pressure. A solid which collected in the condenser and the receiver was probably α -benzyltetronic acid, produced by decomposition of the γ -bromo-ester:



A point of interest has been observed in the case of the halogen derivatives of ethyl acetoacetate. These compounds react with hydrazine hydrate, but the volumes of nitrogen liberated are less than the theoretical amount, the monochloro-compound yielding some 63 per cent., and the monobromo-derivative about 82 per cent., of the calculated quantity. This behaviour may be connected with the basic nature of the reagent, which may stabilise the monochloro- and monobromo-acetoacetates to some extent in the enolic form. This view seems to be supported by the fact that the halogen derivatives of the substituted acetoacetic esters—in which

enolisation cannot take place—react quickly with hydrazine hydrate, nitrogen being liberated quantitatively. Against this view it may be urged that disturbance of the equilibrium will tend to make the compound react entirely in the keto-form, and the low result may be due to secondary reactions such as the formation of ring compounds. Such reaction actually takes place, as corresponding pyrazolones have been isolated from the halogen derivatives of substituted acetoacetic esters, but the formation of the ring compound appears to occur subsequent to reduction, for the evolution of nitrogen is quantitative in the cases examined. Further attention, however, is being devoted to this question.

EXPERIMENTAL.

The estimations referred to in the following cases were carried out in a Van Slyke nitrometer, and 1 c.c. of hydrazine hydrate (50 per cent. solution) was a sufficient excess for the quantities of the halogen compounds used.

Ethyl α -chloroacetoacetate was prepared by the action of sulphuryl chloride (1 mol.) on the molecular quantity of ethyl acetoacetate (Allihn, *Ber.*, 1878, **11**, 567). The chloro-ester boils at $193^{\circ}/760$ mm. with little decomposition, and distils under reduced pressure as a colourless oil, b. p. $88-89^{\circ}/11$ mm., n_D^{20} 1.4420. An alcoholic solution was prepared containing 1.645 grams of the ester in 25 c.c., and 5 c.c. of this solution liberated 15 c.c. N_2 at 17° and 760 mm. The bimolecular quantity therefore liberates 17.74 grams of N_2 on treatment with hydrazine hydrate, or 63.3 per cent. of the chloro-compound reacts.

Ethyl $\alpha\alpha$ -dichloroacetoacetate was prepared by the action of a molecular quantity of sulphuryl chloride on the monochloro-ester. It has b. p. $205-207^{\circ}/756$ mm., $91^{\circ}/11$ mm., and n_D^{20} 1.4492. Five c.c. of an alcoholic solution, containing 0.995 gram of the ester in 25 c.c., on treatment with hydrazine hydrate liberated 23.2 c.c. N_2 at 17° and 760 mm. The molecular quantity therefore liberates 27.4 grams N_2 , or about 97 per cent. of the ester reacts.

Ethyl α -chloromethylacetoacetate is conveniently prepared by the action of sulphuryl chloride on ethyl methylacetoacetate (Roubleff, *Annalen*, 1890, **259**, 254). It has b. p. $81^{\circ}/13$ mm. Five c.c. of an alcoholic solution, containing 1.785 grams of the chloro-ester in 25 c.c., liberated 23.4 c.c. N_2 at 13° and 760 mm. on treatment with hydrazine hydrate. The bimolecular quantity liberates 28.06 grams N_2 , and therefore the compound consists entirely of the α -chloro-ester.

Ethyl α -chloroethylacetoacetate also was prepared by means of sulphuryl chloride, and has b. p. $203-204^{\circ}/770$ mm., $90.5^{\circ}/10$ mm., and n_D^{20} 1.4372. 1.925 Grams were made up to 25 c.c. with alcohol,

and 5 c.c. of the solution liberated 23.6 c.c. N_2 at 16° and 760 mm. when treated with hydrazine hydrate. The bimolecular quantity liberates 28.00 grams N_2 and therefore the compound consists entirely of the α -chloro-ester.

Ethyl α -Chloropropylacetoacetate.—Fifteen grams of ethyl propylacetoacetate were heated to about 40° , the molecular quantity of sulphuryl chloride was gradually added, and the mixture was then heated on the water-bath for upwards of an hour. After washing with water and drying with anhydrous sodium sulphate, the product was fractionated under reduced pressure and distilled in a main fraction at $108-110^\circ/10$ mm. as a clear oil with a faint yellow tinge, n_D^{20} 1.4420 (Found: Cl = 17.4. $C_9H_{15}O_3Cl$ requires Cl = 17.2 per cent.). An alcoholic solution was prepared containing 2.065 grams of the ester in 25 c.c., and 5 c.c. of this solution liberated 23.8 c.c. N_2 at 16° and 756 mm. The ester therefore consists entirely of the α -chloro-compound.

Ethyl γ -bromoacetoacetate was prepared by Conrad's method (*Ber.*, 1896, 29, 1042). On distillation under reduced pressure, the ester had b. p. $115-120^\circ/15$ mm., a value which agrees with the records of Auwers and Auffenberg (*Ber.*, 1917, 50, 950) and Chick and Wilsmore (*T.*, 1910, 97, 1988), but is contrary to the value $125^\circ/40$ mm. recorded by Epprecht (*Annalen*, 1894, 278, 77). An alcoholic solution of the customary strength was prepared, but it liberated no nitrogen on treatment with hydrazine.

Ethyl α -bromoacetoacetate is best prepared by Brühl's method (*Ber.*, 1903, 36, 1731). The ester has b. p. $99-102^\circ/13$ mm., and liberates nitrogen from hydrazine hydrate in the cold, but, as in the case of the chloro-compound, the reaction is not quantitative. 2.09 Grams of the ester were made up to 25 c.c. with alcohol, and 5 c.c. of the solution liberated 19.8 c.c. N_2 at 16° and 750 mm. The bimolecular quantity therefore liberates 23.2 grams N_2 , or about 82.6 per cent. of the bromo-ester reacts. The solution liberated iodine quantitatively from an acidified solution of potassium iodide.

Ethyl $\alpha\alpha$ -dibromoacetoacetate, prepared according to Brühl's method (*loc. cit.*), has b. p. $120-124^\circ/13$ mm. It liberates nitrogen from hydrazine hydrate in the cold, but the values are less than the theoretical amount. Five c.c. of a solution containing 1.44 grams of the ester in 25 c.c. liberate 22.0 c.c. N_2 at 16° and 750 mm. Nearly 92 per cent. of the ester therefore reacts.

Ethyl α -Bromomethylacetoacetate.—14.5 Grams of ethyl methylacetoacetate were placed in a small Dreschel bubbler immersed in ice, and approximately the calculated quantity of bromine was introduced by drawing a current of air through bromine into the

apparatus by means of a suction pump. The current of air was thereafter maintained for fifteen minutes to sweep out hydrogen bromide and the excess of bromine. The crude bromo-ester was repeatedly washed with water containing a little sodium thiosulphate, and after a final washing with water was extracted with ether. The ethereal solution was dried with anhydrous sodium sulphate, and after the removal of the solvent the ester was fractionated under reduced pressure. It distilled in a main fraction, as an almost colourless oil, at $93^{\circ}/10$ mm., n_D^{20} 1.4560. The product is the pure α -bromo-ester, for 5 c.c. of an alcoholic solution, containing 2.23 grams of the ester in 25 c.c., liberated 23.6 c.c. N_2 at 15° and 760 mm. This corresponds with 100.2 per cent. of ethyl α -bromomethylacetoacetate.

Ethyl α -Bromoethylacetoacetate.—Sixteen grams of ethyl ethylacetoacetate were brominated as described in the preceding case. The product consisted of the α -bromo-ester, which has b. p. $106^{\circ}/11$ mm., and n_D^{20} 1.4586. 2.37 Grams of the pure ester were made up to 25 c.c. with alcohol, and 5 c.c. of this solution liberated 23.5 c.c. N_2 at 15° and 760 mm. This corresponds with the theoretical amount required for the pure α -bromo-ester.

If bromination is carried out at the ordinary temperature, some γ -bromo-ester will be formed; in one experiment, estimation with hydrazine hydrate showed that nearly 20 per cent. of the γ -ester was present. The γ -ester is probably the main product formed when the bromination is carried out by means of bromine in chloroform, for Nef (*Annalen*, 1891, 266, 94) has shown that the bromo-ester so obtained is converted in α -ethyltetronic acid and ethyl bromide when heated in a sealed tube at 100° (compare also Wedel, *Annalen*, 1883, 219, 101; Demarey, *Ann. Chim. Phys.*, 1880, [v], 20, 439, 465).

Ethyl α -Bromopropylacetoacetate.—Seventeen grams of the parent ester were brominated by the method described above, and the ester was obtained as a clear yellow oil boiling at $130^{\circ}/10$ mm., n_D^{20} 1.4610 (Found: Br = 31.63. $C_9H_{15}O_3Br$ requires Br = 31.87 per cent.). Five c.c. of an alcoholic solution, containing 2.51 grams of the bromo-ester in 25 c.c., on treatment with hydrazine hydrate liberated 23.7 c.c. N_2 at 16° and 756 mm. This corresponds with 99.82 per cent. of the α -bromo-ester.

Ethyl α -Bromobenzylacetoacetate.—Fifteen grams of the parent ester were brominated in the usual way, and the product was obtained as a pale yellow oil which consisted entirely of the α -bromo-ester. It has b. p. $180^{\circ}/14$ mm. and n_D^{20} 1.5280 (Found: Br = 26.91. $C_{13}H_{15}O_3Br$ requires Br = 26.75 per cent.). Five c.c. of an alcoholic solution, containing 2.99 grams of the bromo-ester in 25 c.c., liberated

23.4 c.c. N_2 at 14° and 758 mm. This corresponds with a percentage purity of the α -ester of 99.5.

Ethyl α -Chloroethylbenzoylacetate (Ethyl α -Chloro- α -benzoylbutyrate).

—The ethyl benzoylbutyrate used in the work was prepared by Hope and Perkin's method (T., 1909, 95, 2042). Ten grams of sulphuryl chloride (1 mol.) were gradually added to 15 grams of the benzoylbutyrate, and after the reaction was complete the product was dissolved in ether and thoroughly washed with water. After drying with sodium sulphate and removal of the solvent, the residual oil was fractionated under reduced pressure and distilled at $156^\circ/14$ mm.; n_D^{20} 1.5108 (Found: Cl = 14.2. $C_{13}H_{15}O_3Cl$ requires Cl = 13.95 per cent.). The chloro-ester liberates iodine from potassium iodide, but the reaction is not quantitative. The ester consists of the pure α -chloro-compound, for 5 c.c. of an alcoholic solution, containing 2.545 grams of the chloro-ester in 25 c.c., liberated 23.6 c.c. N_2 at 15° and 758 mm. The bimolecular quantity therefore liberates 28.03 grams of nitrogen, which corresponds with the amount expected from the pure α -chloro-ester.

Ethyl α -Bromoethylbenzoylacetate (Ethyl α -Bromo- α -benzoylbutyrate).

—The parent ester, when acted upon by bromine vapour introduced in a current of air, is converted entirely into the α -bromo-derivative. The purification is carried out as in the cases previously described, and the ester is obtained as a clear oil with a faint orange tint. It has b. p. $181^\circ/15$ mm. and n_D^{20} 1.5350 (Found: Br = 26.54. $C_{13}H_{15}O_3Br$ requires Br = 26.75 per cent.). The bromo-ester liberates iodine from potassium iodide, but the reaction is not quantitative even after two hours. The reaction with hydrazine hydrate at the ordinary temperature is quantitative, and therefore the ester consists entirely of the α -bromo-compound. An alcoholic solution was prepared containing 2.99 grams of the ester in 25 c.c., and 5 c.c. of this solution liberated 23.6 c.c. N_2 at 16° and 757 mm. The bimolecular quantity therefore liberates 28.00 grams of nitrogen, which is in good agreement with the theoretical value.

γ -Chlorobenzoylacetone.—The chloro-compound was first prepared by the action of chlorine on the copper salt of benzoylacetone, a method which had proved successful in the case of other diketones (Auwers and Aufferberg, *loc. cit.*). The copper salt of the diketone is obtained in almost quantitative yield by shaking an ethereal solution of benzoylacetone with an aqueous solution of copper acetate (Wislicenus and Stoeber, *Ber.*, 1902, 35, 545). The dry copper salt was suspended in carbon disulphide and a stream of chlorine passed in until the precipitation of the copper chloride was complete. After filtration, the carbon disulphide was removed under

reduced pressure, and the residue extracted with ether. The residual oil after removal of the ether was distilled under reduced pressure, and collected in a main fraction boiling at $145^{\circ}/14$ mm.

A more convenient method of preparing the chloro-diketone, and one which gives better yields, is as follows. Forty grams of the diketone are covered with ether and 35 grams (1 mol.) of sulphuryl chloride gradually added with shaking, a brisk reaction with the evolution of sulphur dioxide and hydrogen chloride occurring after each addition. The mixture is then heated on the water-bath for upwards of an hour to complete the reaction, and the residual oil, after being washed with water and dried, is fractionated under reduced pressure. It distils in a main fraction at $142^{\circ}/11$ mm., having n_D^{20} 1.5672. Yield 42 grams, or 85 per cent. of the theoretical amount. The oil obtained on distillation does not solidify even after standing for two months. γ -Chlorobenzoyl-acetone readily forms a copper salt; it also liberates iodine from an acidified solution of potassium iodide, and after standing for a short time the reaction is quantitative. 1.965 Grams of the chloro-diketone were dissolved in 25 c.c. of alcohol, and 5 c.c. of the solution, when added to an acidified aqueous-alcoholic solution of potassium iodide, liberated iodine immediately; after standing for a short time, 39.8 c.c. of N/10-thiosulphate were required for titration, which corresponds with Cl = 17.97 ($C_{10}H_7O_2Cl$ requires Cl = 18.06 per cent.).

Alcoholic solutions of γ -chlorobenzoylacetone do not liberate nitrogen from hydrazine hydrate at the ordinary temperature.

On heating an alcoholic solution of the chloro-diketone with a molecular quantity of *p*-nitrophenylhydrazine, condensation takes place with the formation of 4-chloro-3(or 5)-phenyl-1-*p*-nitrophenyl-5(or 3)-methylpyrazole. After three crystallisations from glacial acetic acid, the pyrazole is obtained as orange needles, m. p. $155-157^{\circ}$ (compare Morgan, Drew, and Barker, *loc. cit.*).

$\gamma\gamma$ -Dichlorobenzoylacetone.—Seventeen grams (1 mol.) of sulphuryl chloride were gradually added to 24 grams of γ -chlorobenzoylacetone, and the product was heated on the water-bath for half an hour. After washing with water and drying, the oil was distilled under reduced pressure and collected in a main fraction boiling at $158^{\circ}/14$ mm. It is a clear, refractive oil, with a faint orange tint, n_D^{20} 1.5530 (Found: Cl = 31.0. $C_{10}H_6O_2Cl_2$ requires Cl = 30.7 per cent.). The yield amounts to more than 80 per cent. of the theory. The dichloro-compound does not form a copper salt, nor liberate nitrogen from hydrazine hydrate at the laboratory temperature. It liberates iodine from acidified potassium iodide, but the reaction is not quantitative even after two hours. Both the chloro-derivatives

of benzoylacetone have lachrymatory properties, but they do not irritate the eyes to nearly the same extent as the corresponding derivatives of acetylacetone.

4-p-Nitrobenzenecazo-3(or 5)-phenyl-1-p-nitrophenyl-5(or 3)-methylpyrazole.—2.3 Grams (1 mol.) of γ -dichlorobenzoylacetone, dissolved in 30 c.c. of alcohol, were added to a filtered solution of 3 grams (2 mols.) of *p*-nitrophenylhydrazine in two litres of water containing a little hydrochloric acid, and the mixture was vigorously shaken. The colour of the solution gradually reddened and after some minutes the pyrazole began to separate as a flocculent, reddish-orange precipitate. The reaction was almost complete after an hour's shaking, but the mixture was kept for another two hours, when the pyrazole was collected and washed well with hot water. It was crystallised once from acetone and several times from aqueous acetone to remove a highly coloured impurity, and was thus obtained as very fine, orange-red needles, m. p. 295–297° (Found: N = 20.2. $C_{22}H_{16}O_4N_6$ requires N = 19.7 per cent.). The substance is moderately soluble in acetone or ether, less soluble in alcohol, and sparingly soluble in glacial acetic acid. It is our intention to study this type of reaction further.

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[Received, January 27th, 1923.]

CXXVII.—*The Labile Nature of the Halogen Atom in Organic Compounds. Part IX. The Electrical Conductivities and the Reduction of Derivatives of Nitroform.*

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ALEXANDER KILLEN MACBETH.

The Electrical Conductivities of Derivatives of Nitroform.

IT has long been known that a large number of organic compounds are to a greater or less degree conductors of electricity when dissolved in liquid sulphur dioxide. The exhaustive researches of Walden (*Z. physikal. Chem.*, 1903, **43**, 385) showed that the equivalent conductivity of such solutions increased with increasing dilution in the same way as the equivalent conductivity of aqueous solutions of electrolytes, and therefore he ascribed the mechanism of conductivity in these cases also to ionisation of the organic compounds concerned. A review of the various substances investigated shows that the power of acting as an electrolyte

depends in a marked manner on the chemical constitution of the compound, one of the most interesting cases being triphenylmethyl, which shows a considerable conductivity in liquid sulphur dioxide (Walden, *loc. cit.*; Gomberg and Cone, *Ber.*, 1904, 37, 2044). The peculiar reactivity of the grouping involved in the union of three phenyl groups to one carbon atom is seen in the conductivity shown by triphenylcarbinol, triphenylmethyl chloride, and triphenylmethyl bromide; methyl bromide and trimethylcarbinol being non-electrolytes. In these so-called abnormal electrolytes the exact mechanism which leads to the formation of ions is not well understood, more especially in a case such as triphenylmethyl where tautomerism may play a very important part in determining the reactivity and the electrical properties, and therefore it seemed to be of interest to investigate the behaviour of the somewhat simpler cases presented by derivatives of nitroform, where the groups are of the same polar type as in triphenylmethyl. It has been shown in the earlier papers of this series that here the possibility of ascribing the remarkable reactivity to tautomeric changes may definitely be ruled out of account. In making the measurements the experimental procedure adopted by Gomberg and Cone (*loc. cit.*) was followed, with the exception that unplatinised electrodes were used in view of Walden's observation that there was danger of platinised electrodes being attacked in the presence of halogen compounds. For purposes of comparison with the nitroform derivatives the conductivities in liquid sulphur dioxide of other representative compounds containing labile halogen were measured. Observations were made for each of the following compounds, of which the first two were used as controls in testing the sulphur dioxide: ethyl bromide, ethylene dibromide, ethyl monobromomalonate, ethyl dibromomalonate, tetranitromethane, chlorotritnitromethane, and bromotritnitromethane. These substances may be sharply divided into two classes, according to the magnitude of their electrical conductivities. Tetranitromethane, chlorotritnitromethane, and the mono- and di-bromomalonic esters gave such small values for their specific and molecular conductivities that they are practically non-conductors in this solvent. It is evident, therefore, that the lability of the halogen atom in these compounds is not accompanied by ionisation in solution in liquid sulphur dioxide. On the other hand, bromotritnitromethane displayed a marked conductivity under similar conditions, and the values of the molecular conductivity were found to increase with the dilution. There is no possibility, however, of interpreting the observations as being due to simple ionisation into ions of Br and $\cdot\text{C}(\text{NO}_2)_3$, for by reference to the tables given in the experi-

mental part it will be seen that the molecular conductivity first increased to a maximum and afterwards fell slowly to a permanent, small value; at this stage a red colour developed in the solution, which then appeared to contain free bromine, the accompanying chemical change being of an exothermic nature. It may be noted in this connexion that previous work has shown the reactivity of the bromine atom in compounds containing labile halogen to be in general more pronounced than that of chlorine under similar conditions. The observed values of the conductivity give a record of the progress of the reaction, which was found to take place equally readily in ordinary glass vessels, and therefore is independent of any possible changes brought about by the passage of the current or by the nature of the electrodes. The low figure for the final conductivity of the highly coloured solution along with the presence of free bromine rendered it advisable to investigate the behaviour of bromine in liquid sulphur dioxide. When highly purified material was used, the conductivities observed were in agreement with those previously recorded by Walden, but it was found that in this case also the value of the conductivity was not constant, but decreased gradually with time until a steady state was reached at the end of about forty minutes. Taking all the facts into consideration, the most probable explanation of the various changes appears to be that bromotrinitromethane, like the corresponding chloro- and nitro-compounds, does not itself function as an electrolyte, but that during the course of the chemical reaction between the bromo-compound and the sulphur dioxide, intermediate, ionised substances are produced. It is significant that the final values recorded for the coloured solution after the reaction are of the same order of magnitude as would be given by small quantities of free bromine. The reaction may be regarded as passing through a stage during which one or more of the components of the system are ionised and finally further changes take place giving an un-ionised product along with very slightly dissociated bromine. A reaction of this type, carried out wholly in a homogeneous system, would proceed until a definite equilibrium position was reached, and the possibility of isolating the products will depend in large measure on the position of this equilibrium. Experiments with larger quantities of material, and therefore necessarily conducted in more concentrated solution, showed, however, that little decomposition of the bromo-compound had taken place at equilibrium, a result only to be expected when the very low value of the maximum conductivity at small dilution is taken into account. The formation of hexanitroethane, with liberation of bromine, from two molecules of bromotrinitromethane

would provide a simple explanation of the observed facts, but with the experimental evidence at present available it is impossible to say whether the failure to isolate any of this compound is to be attributed to the small quantity of it present at the equilibrium point, or to the fact that it had not been formed.

The Reduction of Derivatives of Nitroform.

The reduction of tetranitromethane and the halogen derivatives of nitroform has already been the subject of some study, and it has been shown that alkaline reducing agents, such as hydrazine, remove the halogen atoms from chloro- and bromo-trinitromethane (Macbeth and Pratt, T., 1921, **119**, 1356) and eliminate one of the nitro-groups from the tetranitro-compound (Baillie, Macbeth, and Maxwell, T., 1920, **117**, 889). Further investigations showed that titanous chloride also removed these atoms or groups, and in addition reduced the resulting nitroform to guanidine (Henderson and Macbeth, T., 1922, **124**, 892). The course of the reactions in reductions by this reagent was deduced from a study of the amount of titanous chloride oxidised by the nitro-compounds, and as very dilute solutions of the materials were used in these experiments the yields of guanidine expected were so small that no attempt was made to isolate the product. It therefore seemed desirable to confirm the results of this work by applying other methods of acid reduction, isolating the final product of the reaction, and identifying it as guanidine. Such work is now described. Three methods of reduction were employed, the reactions being effected by (a) nickel-coated zinc and hydrochloric acid, (b) iron with hydrochloric acid as a catalyst, and (c) iron with sulphurous acid present as catalyst. Guanidine was produced in all three cases.

EXPERIMENTAL.

Chloro- and bromo-trinitromethanes were prepared by the action of fuming nitric acid on acetylene, followed by treatment with the halogen or halogen acid (T., 1921, **119**, 354). Tetranitromethane was prepared by the action of fuming nitric acid on acetic anhydride (Chattaway, T., 1910, **97**, 2099). For the conductivity experiments, these compounds were purified by distillation under diminished pressure in presence of silver carbonate, the distillation being repeated immediately before the substance was required for use. The bromotrinitromethane was further purified by crystallisation.

Conductivity Experiments.

The cells used were of the pattern described by Gomborg and Cone (*Ber.*, 1906, **37**, 2044), with unplatinised electrodes, and the

weighed quantities of substances were introduced into the cells in very small, carefully cleaned glass bottles. The sulphur dioxide was distilled directly into the cell and the weight of liquid determined. This was reduced to volume by making use of the density figures given by Walden (*Z. physikal. Chem.*, 1901, **39**, 518). The temperature was in all cases 0°. The Kohlrausch method of measurement with alternating current was used throughout.

κ = specific conductivity of the sulphur dioxide used.

v = volume in litres containing one gram-molecule of solute.

μ = molecular conductivity of the substance at the given dilution.

Substance.	$\kappa \times 10^5$	v	μ
Ethyl bromide	0.123	17.4	0.0057
Ethylene dibromide	0.123	27	0.035
Ethyl monobromomalonate	0.123	39.3	0.074
Ethyl dibromomalonate	0.114	25	0.009
Tetranitromethane	0.148	8	0.000
Chlorotrinitromethane	0.173	17	0.009

All these values were constant and duplicate experiments gave almost identical results.

Bromotrinitromethane.—The maximum molecular conductivity and the time interval before it was attained are printed in italics.

$$v = 4.8, \quad \kappa = 0.236 \times 10^{-5}.$$

Time (mins.)	2	5	10	20	40	70	80
μ	0.25	0.10	0.07	0.05	0.04	0.04	0.03

$$v = 9.8, \quad \kappa = 0.181 \times 10^{-5}.$$

Time (mins.)	2	5	10	20	40	60	1000
μ	0.82	0.63	0.40	0.27	0.18	0.14	0.09

$$v = 32, \quad \kappa = 0.18 \times 10^{-5}.$$

Time (mins.) ...	2	5	10	15	20	25	30	40	1000
μ	0.06	1.8	4.2	4.8	4.2	3.7	3.3	2.5	0.46

$$v = 161, \quad \kappa = 0.404 \times 10^{-5}.$$

Time (mins.)	2	3	5	10	15	20	
μ	0.07	0.26	0.65	1.70	3.08	5.23	
Time (mins.)	25	30	35	40	45	55	1020
μ	0.18	6.75	6.35	6.04	5.8	5.2	1.7

Conductivity of Purified Bromine.—A sample of A.R. bromine was further purified by being shaken with water and with concentrated sulphuric acid. It was kept over pure barium carbonate, distilled over phosphoric oxide, redistilled twice, and stored in sealed glass tubes.

$$v = 10, \quad \kappa = 0.168 \times 10^{-5}.$$

Time (mins.)	2	5	10	20	40
Equivalent conductivity	0.25	0.22	0.19	0.18	0.16

Attempted Isolation of the Reaction Products.

A concentrated solution of bromotrinitromethane in liquid sulphur dioxide developed heat and began to colour after ten minutes at 0°. After twenty-four hours, the solvent was allowed to evaporate away from the red solution, and some of the gas was passed through water, which was then found to give a copious precipitate with barium chloride. The sulphur dioxide alone did not give this reaction, which was therefore due in all probability to the presence of free bromine. When the whole of the solvent had evaporated, a dark-coloured oil remained which froze at 0°; the crystals obtained after a small quantity of adhering oil had been drained away proved to be unchanged bromotrinitromethane. No trace of any compound of higher melting point could be found and, in particular, no hexanitroethane (m. p. 142°) could be isolated.

Reduction of Derivatives of Nitroform.

Reduction with Zinc and Hydrochloric Acid.—Rakshit (*J. Amer. Chem. Soc.*, 1914, **36**, 1221) acted on tetranitromethane with zinc and hydrochloric acid with the object of preparing tetra-aminomethane, but he obtained guanidine. The work was repeated by the authors, with minor modifications of the method, and similar reductions were carried out with chloro- and bromo-trinitromethanes, but in all cases the yields were poor, about 20–23 per cent. of the theoretical amount of guanidine hydrochloride being obtained. A typical experiment may be described. Zinc turnings (200 grams), having been immersed in a dilute solution of nickel sulphate overnight and washed with water, were mixed with 5 c.c. of bromotrinitromethane and 25 c.c. of water, and 4 c.c.-portions of 2N-hydrochloric acid were run in at intervals with continuous shaking. The nitro-compound having disappeared, a further 30 c.c. of acid were added and the mixture, after remaining overnight, was heated on a water-bath until the odour of the nitro-compound could no longer be detected. The liquid was then decanted, the zinc washed several times with boiling water, and sodium carbonate added to the combined liquid and washings. The filtrate from zinc carbonate was acidified with hydrochloric acid and evaporated to dryness, the residue being extracted with rectified spirit. After removal of the solvent, the product was heated under reflux with absolute alcohol and the filtered solution evaporated to dryness. The crude guanidine hydrochloride was heated with a mixture of equal parts of absolute alcohol and ether, and a little vegetable charcoal (merit), and after filtration, removal of the solvent, and drying at 30° in a vacuum, 0.9 gram, or about

21 per cent. of the theoretical amount, of the pure hydrochloride was obtained (Found: Cl = 35.4. Calc., Cl = 36.8 per cent.). The bromo-compound reacted more vigorously than tetranitromethane or chlorotrinitromethane, these yielding about 23 per cent. and 29 per cent., respectively, of the theoretical quantity of guanidine hydrochloride. The chlorine content of the guanidine hydrochloride was in all cases determined by the silver nitrate-thiocyanate method; the results obtained were mostly low, probably on account of imperfect drying of the material.

Reduction with Iron and Hydrochloric Acid.—A process in which 10 grams of tetranitromethane were dropped, with constant shaking, into a cold mixture of 50 grams of iron turnings, 50 c.c. of water, and 5 c.c. of 2*N*-hydrochloric acid having been found to give low yields of guanidine, the method was modified, 5 c.c. of the nitro-compound being added to a mixture of 50 grams of iron filings and 50 c.c. of water, mechanically stirred, and cooled in running ice-water; on the addition of a few drops of 2*N*-hydrochloric acid, reaction commenced and nitrous fumes were evolved, the temperature rising unless the cooling arrangements were efficient. After upwards of an hour the main reaction was over, and the mixture was then heated on a water-bath until the odour of the nitro-compound had disappeared. The sludge was removed and washed several times with boiling water, ammonia added to the combined filtrates and washings, and hydrogen sulphide passed into the alkaline solution to precipitate any iron that had gone into solution (in the best experiments it was found that little iron had dissolved). The filtrate from the iron sulphide was acidified with hydrochloric acid, boiled to expel excess of hydrogen sulphide, the precipitated sulphur removed, and the filtrate evaporated to dryness. The guanidine hydrochloride was isolated from the residue as described in the preceding method. The average yield of guanidine hydrochloride in a series of experiments was about 29 per cent. of the theoretical amount (Found: Cl = 36.7 per cent.).

Chlorotrinitromethane was reduced in a similar way. The average yield, however, was lower, amounting to 32–34 per cent. of the theoretical.

The reaction was very vigorous in the case of the corresponding bromo-compound and very efficient cooling was necessary. The average yield of guanidine hydrochloride was 30 per cent.

Reduction with Iron and Sulphurous Acid.—Tetranitromethane was readily reduced by this method, the procedure being similar to that described in the preceding section. A relatively large quantity of iron and a small amount of sulphur dioxide were

employed. Reduction proceeded rapidly and little iron was left in the solution at the end of the reaction. The reduction product consisted of guanidine hydrochloride, contaminated by traces of the sulphate, the latter resulting from the oxidation of the sulphurous acid employed.

Identification of the Reduction Product as Guanidine Hydrochloride.—On account of the difficulty encountered in removing all traces of water from the products of the various reduction experiments the chlorine content of the samples was generally lower than the theoretical value for guanidine hydrochloride. It therefore seems desirable to submit further proof of the identity of the products with this compound. The reduction product (2 grams) from one of the experiments was converted into guanidine nitrate as follows. The substance was dissolved in the minimum quantity of water and a few drops of concentrated hydrochloric acid, 2 c.c. of concentrated nitric acid were added, and after evaporation of the mixture to about one-fifth of its volume crystals quickly separated on cooling. These were collected and recrystallised from water. The guanidine nitrate thus obtained melted at 214° (compare Ulpiani, D.R.-P. 209431). As further confirmation, the reduction product was converted into a picrate in the usual way; this had no definite melting point, but its nitrogen content was in good agreement with the theoretical value required for guanidine picrate (Found: N = 29.2. Calc., N = 29.16 per cent.).

We wish to record our indebtedness to Miss J. Coupar and to Miss A. McLaren for valuable assistance, and one of us (T. H.) desires to express his thanks to the Department of Scientific and Industrial Research for a grant which enabled him to take part in this investigation.

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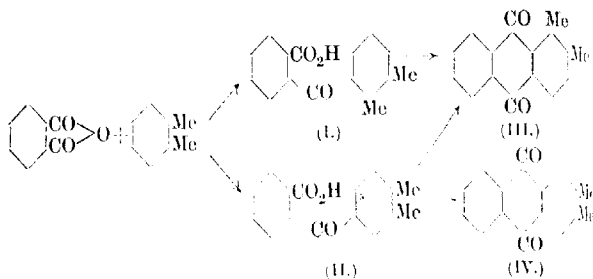
UNIVERSITY OF ST. ANDREWS. *Received, March 13th, 1923.*

CXXVIII.—*Synthesis of 4-Hydroxy-1:2-dimethyl-anthraquinone.*

By ARTHUR FAIRBOURNE and JOHN MILDRED GAUNTLETT.

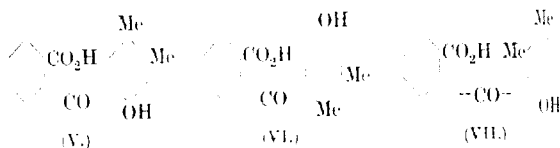
IN continuation of the work previously communicated (T., 1921, 119, 1573), it was decided to attempt to prepare other derivatives of 1:2-dimethylantraquinone, but, if possible, by a method eliminating the troubles of isomerism normally incurred, thus securing independent evidence of the structure of compounds of

the 1:2-dimethyl series (derivatives of III) obtained in reactions such as those described in the previous paper (*loc. cit.*, p. 1574).



It is obvious that if position 5 in the *o*-4-xyloyl radicle (II) be occupied, then the only possible dehydration of the intermediate *o*-xyloylbenzoic acids must yield only the (4-substituted) 1:2-dimethylantraquinone (III).

The synthesis of 4-hydroxy-1:2-dimethylantraquinone was therefore attempted in this way, since it was known that phenols had been successfully condensed with phthalic acid by means of boric acid (Bentley, Gardner, and Weizmann, T., 1907, **91**, 1635). Three different acids, corresponding with I and II above, can result from the condensation of phthalic anhydride and *o*-4-xylenol.



but of these, only the first two, V and VI, are capable of condensation to a three-ring system, and moreover, the formation of the same hydroxyanthraquinone must result in each case. Actually only one acid has been isolated, and this is presumed to be the first of the three, V, since Bentley, Gardner, and Weizmann (*loc. cit.*) have shown that such condensations with boric acid take place only in the ortho-position to the phenolic group, in which circumstances the second acid shown above could not be formed. Moreover, the third formula cannot apply, since dehydration of this acid to give a member of the three-ring system would obviously be impossible.

EXPERIMENTAL.

o-2-Hydroxy-4:5-dimethylbenzoylbenzoic Acid. Equal quantities (10 grams) of boric acid, phthalic acid, and *o*-4-xylenol were heated

at 160° for four hours, and the reddish-brown product was poured into an excess of water and steam-distilled until no more xylenol or boric acid appeared in the condensate. The residue, consisting of substituted benzoylbenzoic acid, unchanged phthalic acid, and any xylenolphthalein formed, was separated by filtration while hot, washed with hot water, and repeatedly boiled with calcium carbonate, the combined filtered extracts finally being concentrated and then acidified with dilute hydrochloric acid. The acid so obtained crystallised from alcohol in small, white needles, m. p. 175° (Found: by titration with $N/10$ -baryta, equivalent = 270, 269. $C_{16}H_{14}O_4$ requires equivalent = 270). The structure of the acid has already been discussed in the theoretical portion.

4-Hydroxy-1:2-dimethylantraquinone.—The dehydration was carried out in the usual way (compare previous paper, *loc. cit.*, p. 1577) except that it was found advisable not to raise the temperature above 100°. The condensed acid was mixed with ten times its weight of concentrated sulphuric acid and heated at 100° for an hour. The dark red solution obtained was poured on to broken ice, and the precipitated quinone collected, filtered, washed, and dried. Several recrystallisations of this substance from acetone gave small, feather-like clusters of golden needles melting at 169° (Found: C = 75.84, 76.00; H = 4.64, 4.72. $C_{16}H_{12}O_3$ requires C = 76.49; H = 4.76 per cent.).

It is expected that by this method of synthesis the various derivatives from 1:2-dimethylantraquinone required will be obtained very much more conveniently than by the process described in the previous paper, their constitutions being also much more clearly defined. Methods for the removal of the radicle in position 4 are under investigation.

KING'S COLLEGE, LONDON.

[Received, March 3rd, 1923.]

CXXIX.—*Investigation of the Mannan Present in Vegetable Ivory.*

By JOCELYN PATTERSON.

VEGETABLE ivory, the endosperm of the seed of the tagua pahu, has long been known as the most convenient source for the preparation of mannose. This sugar always occurs in nature in the form of polysaccharide-like condensation products termed mannans or mannans, which on hydrolysis yield the simple hexose. It is not surprising to find that in the past attention has been directed to the study of the products arising from the complete

hydrolysis of vegetable ivory, rather than to the more difficult subject of the nature of the actual components of vegetable ivory itself or to that constituent from which mannose is derived. Patient research on the latter topics has only revealed for the most part scanty and indefinite information, which it will be convenient to summarise before proceeding to describe the results of the present investigation.

By extracting vegetable ivory with cold 75 per cent. sulphuric acid, Reiss (*Ber.*, 1889, 22, 610) obtained a carbohydrate, called by him seinin, which on hydrolysis with acids yielded a reducing sugar, subsequently proved by Fischer (*Ber.*, 1889, 22, 1155) to be mannose. Later Johnson (*J. Amer. Chem. Soc.*, 1896, 18, 214) extracted vegetable ivory with 10 per cent. potassium hydroxide, and obtained a substance of the composition $C_6H_{10}O_5$, which on hydrolysis gave mannose. Soon afterwards Baker and Pope (*I.*, 1900, 77, 676) described the isolation from vegetable ivory of a substance they termed lavulo-mannan. They extracted by means of 5 per cent. caustic soda and precipitated from the solution by addition of Fehling's solution a blue copper compound, subsequently decomposing this with hydrochloric acid. The ensuing product gave analytical figures for $C_6H_{10}O_5$ and on hydrolysis yielded a syrup 90 per cent. of which was convertible to mannosephenylhydrazine, the remainder being considered to be chiefly fructose. Examining vegetable ivory for other constituents, Iwanoff (*J. Landw.*, 1908, 55, 217) detected small percentages of pentosan and methylpentosan, as well as a trace of araban. He also showed that apart from mannose, which was present in two modifications, as hemicellulose and mannocellulose, no other hexose was present in appreciable quantity. One of these celluloses was subsequently shown by Pringsheim (*Z. physiol. Chem.*, 1912, 80, 376) to be hydrolysed by the action of a bacterial infusion acting on the ivory meal itself, giving rise to mannose and a trisaccharide, considered to be a trimannose, which was isolated in the form of its phenylosazone.

The above account shows the position which had been reached in the investigation of vegetable ivory when the work proceeding in this laboratory on polysaccharides was extended to include the mannan occurring in the natural product, and the present paper deals with the results so far obtained. The work now described had just been completed when a paper covering a portion of the same field of research was published by Pringsheim and Seifert (*Z. physiol. Chem.*, 1922, 123, 205), who in resuming their work on hemicelluloses undertook a more detailed study of the mannan present in vegetable ivory. Taking advantage of a recently devised general method due to Schmidt and Graumann (*Ber.*, 1921, 54, [B], 1860)

of using chlorine dioxide for the removal of the incrustive substance from plant products without attacking the carbohydrate present, they proceeded to isolate mannan by extracting the "cleaned" residue with 5 per cent. caustic soda. By this means, it appears that the mannan present as hemicellulose was extracted, whilst the residue consisted of mannocellulose.

There can be no doubt that the product the above authors obtained is not identical with that isolated in the present investigation where a somewhat different method of extraction was adopted. This treatment consisted in first removing nitrogenous and resinous matter along with pentosans from the meal by a preliminary treatment with hot 10 per cent. sodium hydroxide and then extracting the "cleaned" material in a series of operations with 20 per cent. alkali. A polysaccharide-sodium hydroxide complex was first isolated by precipitation with alcohol, and subsequently decomposed by dilute acetic acid to give the polysaccharide itself. It is obvious that the preliminary treatment would also remove most, if not all, the mannan which was collected by Pringsheim as well as the products isolated by the earlier workers, as, for example, the "levulomannan" of Baker and Pope. Whilst Pringsheim's compound is the modification of mannan described by Iwanoff as hemicellulose, the present research deals essentially with mannan in the form of mannocellulose.

This substance, which will be simply termed "mannan," was a white powder which required to be heated at 120° in a vacuum in order to be entirely freed from moisture, but which in the ordinary course of drying displayed a tendency to form into granules with a hard, horny surface. It was obtained practically ash-free, had no definite melting point, and did not commence to darken until 210° , the substance being almost completely decomposed at 280° . It was insoluble in all solvents with the exception of concentrated alkali. Like the better known polysaccharides, it conforms to the anhydro-type of the general formula $(C_6H_{10}O_5)_x$.

The extraction of vegetable ivory in the way described can scarcely give even an approximate idea of its actual content of mannan, for besides the amount actually isolated, ranging from 8—10 per cent. of the original material, a certain amount, of which no accurate estimate can be made, is lost in the preliminary treatment with sodium hydroxide. Moreover, it was found that the extracted residue still contains mannan to the extent of 1.5—2 per cent. of the original weight of meal. It will be seen from these figures, however, that the content of mannan is much greater than would be gathered from the amount (4 per cent.) of crystalline mannose obtainable by the direct hydrolysis of vegetable ivory in

the manner recommended by Hudson (*J. Amer. Chem. Soc.*, 1917, 39, 470). The discrepancy is readily accounted for by the fact that the drastic conditions required to attack the material and effect hydrolysis militate against good yields of crystalline sugar.

So far as can be ascertained, mannan is based entirely on mannose residues, no other sugar or its derivative having been detected in the course of investigations on (i) the direct hydrolysis of the polysaccharide by aqueous acid, (ii) the hydrolysis of the polysaccharide by means of acid methyl alcohol, (iii) the decomposition of the triacetate by means of acid methyl alcohol, and (iv) the hydrolysis of methylated mannan.

Unfortunately, the quantitative aspect of this work was greatly hampered by the extraordinary stability of the polysaccharide. This may be partly due to its physical condition, the horny surface covering the grains being extremely resistant to attack. From the purely quantitative point of view, the most satisfactory result was that obtained by the direct aqueous hydrolysis of the polysaccharide. Some difficulty was experienced in obtaining the mannose in a crystalline condition when sulphuric acid was used as the hydrolytic agent, but when this was followed by prolonged treatment with dilute hydrochloric acid the crystalline sugar was obtained readily, the yield being 80 per cent. of the theoretical amount.

Unlike starch, which is easily converted into methylglucoside by heating with acid methyl alcohol, mannan was not readily attacked by this agent, and much more drastic conditions than it is necessary to employ on the better known polysaccharides were required. It was found, however, that such portion of the mannan as took part in the hydrolysis was converted entirely into methylmannoside, which readily crystallised as being largely of the α -form. The major portion of the polysaccharide was unaffected by this treatment, and was recovered unchanged.

The attempt made to bring about a quantitative conversion of the polysaccharide to methylmannoside by first preparing its triacetate and subsequently hydrolysing this by means of acid methyl alcohol was equally unsuccessful. In this case also, the substance showed marked stability towards the usual acetylating reagents. The method of Barnett (*J. Soc. Chem. Ind.*, 1921, 40, 8r), which depends on the use of sulphuryl chloride, was found to be more satisfactory than those involving zinc chloride and sulphuric acid as catalysts. Before these latter become operative the temperature has to be elevated to an extent which results in decomposition and hydrolysis. Even under the best conditions, the acetylation could not be made to proceed quantitatively, there being always a large percentage of mannan which resisted pro-

longed attack. The product of the reaction was a white, amorphous solid, melting indefinitely at 128–145°, which corresponded in composition to mannan triacetate, $C_6H_7O_5(CO-CH_3)_3$.

Once obtained, this substance was readily and quantitatively convertible into methylmannoside, which, as before, crystallised at once, the α -form being in large excess.

The further investigation of mannan was concerned with the two basic factors of its constitution, namely, the type of sugar (stable form or γ -form) to which the hexose units conform and the manner in which these units are combined. To solve both aspects of the constitutional problem, recourse must be made to methylation, the application of which process has been fully discussed in previous papers issued from this laboratory, and need not be detailed here. Mannan, on being subjected to repeated alkylations by means of methyl sulphate and sodium hydroxide, yielded a substance corresponding to a dimethyl mannan after four treatments. Three further operations raised the methoxyl content to 41 per cent., after which stage it became difficult to methylate further. In the course of three final alkylations, the methoxyl content of the isolated product reached 42.6 per cent., the substance then corresponding closely to a trimethyl mannan. This was obtained in the form of a slightly yellow, amorphous, somewhat hygroscopic powder, which was insoluble in ether, but soluble in chloroform, ethyl acetate, acetone, or benzene, and displayed a marked tendency to form a jelly in these solvents, particularly in chloroform.

It was hoped that some idea of the number of anhydro-hexose units constituting mannan would be obtainable from the molecular weight of methylated mannan, but this property of readily forming jellies with solvents prevented any trustworthy determination being made, and the figures which resulted varied over a very wide range. The peculiar behaviour of the substance would suggest, however, either exceedingly large molecules, or a high degree of polymerisation of simple units.

For some reason which has not yet been elucidated, the methylated mannan, when treated in the usual way, and afterwards more drastically, with acid methyl alcohol, failed to give a quantitative yield of the corresponding methylated methylmannoside, so that the resulting syrup was ultimately hydrolysed by aqueous acid to give the corresponding methylated mannoses. Analysis showed that the substance thus obtained was almost wholly trimethyl mannanose, $C_6H_9O_5(OMe)_3$, and its further investigation as described in the experimental part proves that the material was not a mixture of alkylated mannoses varying from tetramethyl mannanose to dimethyl mannanose, and giving the average composition of a trimethyl

hexose. This particular trimethyl mannose, which was not further purified by distillation, was an almost colourless, fairly viscous, levorotatory syrup.

The levorotation of trimethyl mannose was unexpected; all other mannose derivatives encountered in the course of the investigation being dextrorotatory. A possible interpretation would have been to suppose that this particular compound belonged to the γ -type, but against this view is to be placed the marked stability of the polysaccharide itself, which, if based on γ -mannose residues, would be expected to undergo hydrolysis easily. The nature of the trimethyl mannose under examination was readily determined by its conversion in two stages, both of which involved almost quantitative reactions, to crystalline tetramethyl α -methylmannoside, which is regarded as the best reference substance of the stable type of mannose. The whole of the mannose residues were thus shown to conform to the ordinary or stable type.

Discussion of Results.

The foregoing results need be discussed only in so far as they throw light on the constitution of mannan, which conforms to the ordinary type of polysaccharide of the general formula $(C_6H_{10}O_5)_x$, where x , to judge from the behaviour of the substance itself as well as its fully methylated derivative, must be very large. All the reactions conducted on the substance have yielded mannose or derivatives of mannose, no other sugar having been detected. Despite the fact that the weighable quantities of products obtained from these reactions fall short of the theoretical amount required on the basis of mannan being composed entirely of mannose residues, the results seem to justify the conclusion that the polysaccharide is wholly a polyanhydro-mannose. Moreover, the fact that the hydrolysis of trimethyl mannan led simply to a trimethyl mannose and not to a mixture ranging from tetramethyl mannose to dimethyl mannose, proves that each hexose molecule loses two hydroxyl groups in forming the polysaccharide, leaving the remaining three hydroxyls free for methylation. Again, since trimethyl mannose was entirely convertible to the tetramethyl methylmannoside, identical with that obtained by the methylation of α -methylmannoside, it is evident that all the mannose residues conform to the stable type of sugar.

These facts alone, however, are insufficient to establish the constitution of the polysaccharide, for as yet nothing can be said on the question whether the trimethyl mannose is a single individual or a mixture of isomerides differing in the position of the methyl groups. Both the sugar and its corresponding methylmannoside

were syrups which did not crystallise, and so the individual nature of the sugar itself is not as easily determined as in the case of starch and cellulose, which under similar conditions yield a crystalline trimethyl glucose. Then, again, information on the orientation of the methyl groups in trimethyl mannose is not yet available, so that nothing can be deduced as to the manner in which the hexose residues are united.

The further investigation of mannan will be continued in the direction of providing the necessary data on these two fundamental points, whilst the possibility is not overlooked that there may exist a disaccharide—related to mannan as maltose is to starch or as cellobiose is to cellulose—the constitution of which would also have important bearing on this structural problem. It is obvious, therefore, that, with so many essentials lacking, it would be idle to assign even a provisional constitution to mannan, on the basis of the results obtained up to the present time.

EXPERIMENTAL.

The Preparation of Mannan.—Vegetable ivory meal was first subjected to a preliminary treatment with five times its weight of 10 per cent. sodium hydroxide for half an hour, and was freed thereby from a large quantity of tarry and resinous material. The black, alkaline liquor was filtered off through fine copper gauze and the residual meal carefully washed with hot water. To this residue was added five times its weight of 20 per cent. sodium hydroxide, which was boiled for half an hour, when the solution was again filtered, and about one-third of its volume of rectified spirits added to throw down the sodium hydroxide-polysaccharide complex as a light, gelatinous precipitate. After carefully filtering off this substance and washing with rectified spirits, it was dissolved in hot water and dilute acetic acid added until the whole was just acid. On boiling for a few minutes, the polysaccharide itself was precipitated as a white powder. By repeating this sodium hydroxide extraction process on the residual meal, a further amount of substance was obtained and material could still be extracted even after repeating the operation on the meal eight times. After that, however, the yield of substance became so small as to make the continued extraction not worth the extra time and labour expended.

The product from the first two or three extractions discoloured on drying owing to the presence of impurities, and so it became necessary to repeat the alkali extraction on the substance itself to obtain a pure ash-free product. The yield of mannan was 8–10 per cent. of the original dry meal (Found: C = 44.57; H = 6.30. $C_6H_{10}O_5$ requires C = 44.44; H = 6.17 per cent.).

Aqueous Hydrolysis of Mannan.—Five grams of pure mannan were hydrolysed under the conditions employed by Hudson (*loc. cit.*) on ivory meal. With the exception of a small residue, the whole gradually passed into solution. The acid was neutralised with barium carbonate, the precipitated barium sulphate filtered off, and the excess solvent removed under diminished pressure, yielding as product a clear, stiff, yellow syrup, $[\alpha]_D + 3.9^\circ$ in water. Nucleation of the syrup, dissolved in a small quantity of absolute alcohol and glacial acetic acid, failed to induce crystallisation, even after long standing.

Condensation with aniline after the manner of Irvine and McNicoll (I., 1910, **97**, 1449), which with pure mannose proceeds quantitatively, applied to 1 gram of syrup, yielded 0.45 gram of crystalline mannoseanilide (m. p. 181°), corresponding to a content of 33 per cent. of mannose. Considering that the low percentage of mannose may have been due to the sulphuric acid having caused some liberated mannose to condense with itself, it was decided to continue the hydrolysis using dilute hydrochloric acid, the whole of the syrup being now treated with 5 per cent. acid for eighteen hours. By this means the specific rotation was raised to $+10^\circ$, and on allowing the isolated syrup to stand it slowly solidified to a hard, crystalline mass. Yield = 4 grams. When this hard solid was broken up and carefully washed with glacial acetic acid, white crystals of mannose of m. p. $131-133^\circ$ resulted.

Hydrolysis of Extracted Residue.—In order to determine the equivalent of mannose present in the exhausted residue, 6 grams of this material were hydrolysed by the same method as was applied to mannan. A small amount remained insoluble after hydrolysis with sulphuric acid, whilst the subsequent treatment with hydrochloric acid threw down an appreciable quantity of black, humus-like material. The process yielded a stiff syrup strongly reducing towards Fehling's solution, but which failed to crystallise. Yield about 70 per cent. of the weight of the original material.

Condensation with aniline applied to 1 gram of syrup yielded 0.22 gram of mannoseanilide, indicating that 16 per cent. of the syrup existed as free mannose. Whilst the reaction with aniline proceeds nearly quantitatively with pure mannose, nothing is definitely known as to how far the presence of other syrup inhibits the condensation, so that the percentage given must be regarded as a minimum.

Preparation of Mannan Triacetate.—In a typical experiment, using Barnett's method, 4 grams of mannan were vigorously stirred in a mixture of 25 c.c. of acetic acid and 50 c.c. of acetic anhydride containing sulphuryl chloride as catalyst, the temperature being main-

tained at 70°. It was found advisable to renew the supply of sulphur dioxide and chlorine every four hours, for the action was extremely slow, little more than 1 gram of substance having been reacted upon in twenty-four hours. Isolating in the usual way at the end of this period, 1.6 grams of mannan triacetate were obtained in the form of a white, amorphous powder, of indefinite melting point, 128–145°, and $[\alpha]_D - 3.0$ in chloroform [Found: C = 49.79; H = 5.63. $C_6H_7O_3(CO\cdot CH_3)_3$ requires C = 50.00; H = 5.55 per cent.].

An acetyl estimation by titration with standard sodium hydroxide, in which correction by a control experiment had to be made for the partial solubility of the "regenerated mannan" in alkali, gave $CH_3\cdot CO = 44.7$, 44.4 per cent. [$C_6H_7O_3(CO\cdot CH_3)_3$ requires $CO\cdot CH_3 = 44.8$ per cent.].

Hydrolysis of Triacetate to Methylmannoside.—Two grams of mannan triacetate were hydrolysed by means of methyl alcohol containing 1 per cent. of hydrogen chloride, heated to boiling point under a reflux condenser. The acetate slowly passed into solution and the reaction was completed in eighteen hours, yielding a viscous, non-reducing syrup which quickly crystallised; $[\alpha]_D + 68.6^\circ$ in water [Found: OMe = 15.5. Methylmannoside, $C_6H_{11}O_5(OMe)$ requires OMe = 15.9 per cent.]. The crystals, washed free from the small quantity of adhering syrup (β -methylmannoside) by means of cold methyl alcohol, melted at 189° and did not depress the melting point of an authentic specimen of α -methylmannoside. Total yield of methylmannoside (α - and β -) obtained = 95 per cent. of the theoretical.

Hydrolysis of Mannan to Methylmannoside.—Milder conditions having failed to produce any result, 2 grams of mannan were heated in a sealed tube at a temperature of 140° for seventy-two hours with methyl alcohol containing 7.5 per cent. of hydrogen chloride. In that time a dark brown solution had formed, while more than half of the original material remained unchanged. The product from the alcoholic solution was a stiff, non-reducing syrup which crystallised readily when nucleated with a specimen of α -methylmannoside; $[\alpha]_D + 74.0^\circ$ in ethyl alcohol (Found: OMe = 14.4 per cent.).

Preparation of Trimethyl Mannan.—Mannan, of which 12 grams were used, was dissolved in 25 c.c. of boiling sodium hydroxide (40 per cent.), and after cooling was methylated under the same conditions as were applied to inulin (Irvine and Steele, T., 1920, 117, 1474). The product was isolated along with sodium methyl sulphate by exactly neutralising with dilute hydrochloric acid, taking to dryness under diminished pressure, and then extracting the residue with rectified spirits. The extract was methylated in

the same way three times more, when the substance of methoxyl content equal to 33 per cent. became soluble in chloroform. This solvent was used for extracting the methylated mannan from inorganic material in the three further alkylations, which sufficed to raise the amount of methoxyl to 41 per cent. As the percentage of methoxyl increased, the substance increased its tendency to form a jelly in solvents, which fact made its manipulation exceedingly difficult, and loss of product unavoidable. The process of methylation was finally repeated three times, making ten methylations in all, when the product attained to a methoxyl content of 42.6 per cent. Yield = 5 grams.

Hydrolysis of Trimethyl Mannan. Trimethyl Mannose.—A hydrolysis with acid methyl alcohol to produce a methylated methylmannoside was first attempted. The substance was dissolved in methyl alcohol containing 1.8 per cent. of acid, and boiled under the reflux condenser for forty-two hours. At the end of this period, the isolated product was a fairly mobile syrup, the analytical figures for which did not correspond, however, to a quantitative conversion of trimethyl mannan to trimethyl methylmannoside. More drastic conditions such as the prolonged action of 1 per cent. acid methyl alcohol in a sealed tube at 100° , and treatment with methyl alcohol saturated with hydrogen chloride, did not give the expected product. The syrup was therefore submitted to aqueous hydrolysis with 8 per cent. hydrochloric acid, the action of which was complete in one hour. After neutralising with lead carbonate, removing the precipitate, and evaporating the filtrate to dryness under diminished pressure, the residue was extracted with chloroform. The solution, having been filtered from inorganic material, was evaporated, leaving a fairly viscous, yellow syrup, n_D^{20} 1.4780, $[\alpha]_D^{20}$ -5.8° in water [Found: for the undistilled material, C = 48.4; H = 8.30; OMe = 39.4. $C_6H_{10}O_5(OMe)_3$ requires C = 48.64; H = 8.10; OMe = 41.9 per cent.].

To show that this substance, corresponding so nearly in composition to a trimethyl mannose, was not a mixture ranging from tetramethyl mannose to dimethyl mannose with its constituents in such proportions as to possess this same composition, the whole of the syrup was dissolved in 40 c.c. of water and extracted several times in a separating funnel with 10—15 c.c. of chloroform, a process which removes all the tetramethyl hexose together with a very slight amount of trimethyl hexose from a mixture of the two. Only 8 per cent. of the whole syrup was thus extractable, but neither this extract, nor that part of it soluble in boiling light petroleum, corresponded to tetramethyl mannose. This latter sugar is known to form a well-defined, crystalline anilide on condensation with

aniline, but on conducting the condensation with the extracted syrup, no such compound resulted.

Conversion of Trimethyl Mannose to Crystalline Tetramethyl α -Methylmannoside.

Stage I. Condensation with Methyl Alcohol.—The syrup not extractable by chloroform in the last operation was condensed with methyl alcohol containing 0.5 per cent. of hydrogen chloride, the reaction being conducted in a sealed tube at 100° for eighteen hours, in which period a constant specific rotation was attained of +44.7°. Isolating the product in the usual manner, and using chloroform as its final solvent, it was found to be a mobile, nearly colourless syrup, which distilled to the extent of 95 per cent. of its weight at a pressure of 0.6 mm. and a bath temperature of 135–140°. The colourless, mobile distillate was almost wholly composed of trimethyl methylmannoside, $[\alpha]_D +43.2^\circ$ in methyl alcohol, n_D 1.4616 (Found: OMe = 49.6. Trimethyl methylmannoside requires OMe = 52.4 per cent.).

Dimethyl methylmannoside was apparently present in the residue (OMe = 45.3 per cent.) and a slight amount of this substance would be associated with the distillate.

Stage II. Methylation.—The mannoside was twice methylated by means of silver oxide (3 mols.) and methyl iodide (6 mols.), the product being then isolated and distilled. In this way, tetramethyl methylmannoside was obtained, in practically quantitative amount, as an extremely mobile, colourless syrup, b. p. 105–108°/0.4 mm., n_D 1.4464 (Found: OMe = 60.0. Tetramethyl methylmannoside requires OMe = 62.5 per cent.). This syrup crystallised at once on nucleation with a specimen of tetramethyl α -methylmannoside. After draining on tile to remove the slight amount of the syrupy β -isomeride, the crystals melted at 37–38°, identical with the recorded figure for tetramethyl α -methylmannoside.

In conclusion, the author wishes to express his most grateful thanks to Principal Irvine, who suggested the topic, for his kindly advice and keen interest in the work, and also to the Department of Scientific and Industrial Research for a grant which enabled him to pursue the investigation.

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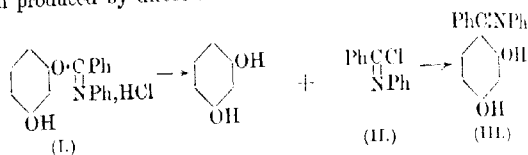
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[Received, March 19th, 1923.]

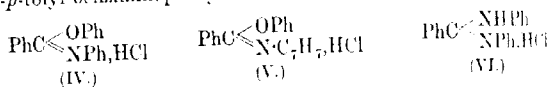
CXXX.—*Imino-aryl Ethers. Part II. The Thermal Decomposition of N-Arylaryliminoaryl Ether Hydrochlorides.*

By ARTHUR WILLIAM CHAPMAN.

IN a previous communication (T., 1922, **421**, 1676), the formation of the anil of benzoylresoreinol (III) on heating the hydrochloride of *N*-phenylbenzimino-*m*-hydroxyphenyl ether (I) was described. It was suggested that this reaction takes place in two stages, the first being the decomposition of the imino-ether hydrochloride into resoreinol and benzanilidiminohydrochloride (II), the ketone anil being then produced by direct substitution in the nucleus:



In order to confirm this suggestion, it appeared desirable to investigate the behaviour of other members of the same series, and for this purpose the hydrochlorides of *N*-phenyl- (IV) and *N*-*p*-tolyl-benziminophenyl ethers (V) were chosen.



These imino-ethers had been previously prepared by Hamisch (Ber., 1893, 26, 926), who also obtained, but did not study, their hydrochlorides.

hydrochlorides. For this investigation, the imino-ethers were prepared by Hantzsch's method, and also by the modification employed by the present author (*loc. cit.*) in the case of *N*-phenylbenzimidazole-hydroxyphenyl ether. The hydrochlorides were obtained pure by passing dry hydrogen chloride into ethereal or benzene solutions of the respective imino-ethers.

A series of experiments was then carried out in which samples of *N*-phenyl-*N*-methylphenyl ether hydrochloride (IV) were heated for times varying from one to two hours at 150–170°. During the early part of the heating, hydrogen chloride was evolved. The most important product was the free imino-ether. The yields of pure material varied from 18 to 37 per cent. of the calculated amount. When allowance is made for the loss of imino-ether involved in its separation from the other substances, a 50 per cent.

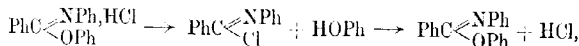
yield is probably a safe estimate in the more favourable cases. The product of next importance was the hydrochloride of diphenylbenzenylamidine (VI), which was identified by conversion into the free base and direct comparison with an authentic specimen. The yield varied considerably, but averaged 18 per cent. A deposit of phenol was always observed on the sides of the reaction tube. Small traces of benzanilide and of phenyl benzoate were also found in some cases.

In contrast to *N*-phenylbenziminophenyl ether hydrochloride, hydrolysis with hydrochloric acid of the melt obtained after heating *N*-phenylbenziminophenyl ether hydrochloride yielded no hydroxybenzophenone; an observation which has its analogy in the circumstance that phenol does not undergo the Hoesch reaction with benzonitrile.

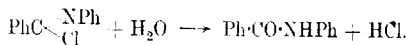
When a mixture of benzanilideiminochloride and phenol in molecular proportions was heated under similar conditions, it yielded a series of products identical with that from *N*-phenylbenziminophenyl ether hydrochloride.

A similar series of experiments on *N*-*p*-tolylbenziminophenyl ether hydrochloride gave completely analogous results, the products being *N*-*p*-tolylbenziminophenyl ether, di-*p*-tolylbenzenylamidine hydrochloride, benzo-*p*-toluidide, phenol, and hydrogen chloride.

If these imino-ether hydrochlorides on heating undergo decomposition into phenol and the anilideiminochlorides, the formation of the free imino-ethers and of the small quantities of anilides can readily be explained. The former will be produced by recombination of the iminochloride and phenol with the evolution of hydrogen chloride at the high temperature,



and the latter by the action of traces of water on residual unchanged iminochloride during the working up of the products:



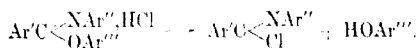
No completely satisfactory explanation of the formation of the amidine hydrochlorides has been found, and this question is undergoing further investigation.

Whilst the observations on the two imino-phenyl ethers were thus in accordance with the view that their hydrochlorides decompose on heating into phenol and the anilideiminochlorides, it seemed desirable to obtain direct experimental proof of the suggestion. For this purpose, advantage was taken of the difference in the boiling points of phenol and benzanilideiminochloride.

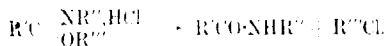
A quantity of *N*-phenylbenziminophenyl ether hydrochloride was heated under reduced pressure in a current of dry hydrogen chloride, the object of the latter being to keep any reformed imino-ether in the state of its hydrochloride. This treatment yielded four fractions of distillate, which were examined by conversion into crystalline derivatives. The first fraction contained phenol and some imino-ether. The imino-ether was probably formed as hydrochloride by condensation of phenol in the receiver with benzanilideiminochloride vapour carried over with it. For quantitative purposes, therefore, the imino-ether was considered as representing the corresponding weights of phenol and benzanilideiminochloride. The second and third fractions consisted of benzanilideiminochloride, but the composition of the small fourth fraction of high boiling point could not be completely determined. Apparently it contained benzanilideiminochloride and the corresponding imino-ether.

In the two distillation experiments performed, the total yield of benzanilideiminochloride were 63 and 52 per cent., and of phenol 33 and 35 per cent., of that calculated from the quantity of imino-ether hydrochloride employed.

It would seem, therefore, that the main first products of the thermal decomposition of *N*-arylaryliminoaryl ether hydrochlorides are the corresponding phenols and anilideiminochlorides:



It appears probable that this type of decomposition is characteristic of the hydrochlorides of imino-aryl ethers in general; whereas the hydrochlorides of imino-alkyl ethers decompose on heating into the corresponding amides and alkyl chlorides (compare Pinner, "Die Imidoäther," 1892; Landor, *T.*, 1901, **79**, 690; 1902, **81**, 591; 1903, **83**, 320, 766):



In view of this contrast, the investigation is being extended to other classes of imino-aryl ethers which do not appear to have been previously prepared.

EXPERIMENTAL.

N-Phenylbenziminophenyl Ether Hydrochloride.—*N*-Phenylbenziminophenyl ether (15 grams) was dissolved in cold dry benzene (150 c.c.) and a current of dry hydrogen chloride passed into the solution. The hydrochloride was precipitated as a pale yellow,

crystalline powder (yield 75 to 80 per cent. of the theoretical) and was dried in a vacuum desiccator over sulphuric acid and solid sodium hydroxide. It melted at $130-132^{\circ}$ with decomposition, and was analysed by repeated extraction with hot dilute nitric acid and estimation of the hydrochloric acid in the combined filtrates (Found: $\text{HCl} = 11.8$. $\text{C}_{19}\text{H}_{15}\text{ON}, \text{HCl}$ requires $\text{HCl} = 11.8$ per cent.).

Separation of the Products of Heating N-Phenylbenziminophenyl Ether Hydrochloride.—Numerous experiments were performed, all the results being in agreement. One separation only is described.

N-Phenylbenziminophenyl ether hydrochloride (6 grams) was heated in an oil-bath at $160-170^{\circ}$, a gentle stream of carbon dioxide being passed through the tube to carry off the hydrogen chloride and prevent the darkening which occurred when the heating was done in the air. The hydrochloride melted and evolved hydrogen chloride during the first half-hour. A slight deposit of phenol formed on the cool upper walls of the tube. After one hour, the brown melt was cooled and extracted with hot benzene. The residue (0.60 gram) was a yellow, crystalline powder, the hydrochloride of a base. It was converted into the free base, which crystallised in beautiful prisms (m. p. $146-147^{\circ}$) identical with an authentic sample of diphenylbenzylamidine. The benzene extract was evaporated and the residue crystallised from alcohol, yielding *N*-phenylbenziminophenyl ether (0.96 gram, m. p. $102-103^{\circ}$), which on recrystallisation melted at $104-105^{\circ}$, and was identical with an authentic specimen. The mother-liquors on evaporation and extraction with ether yielded a further quantity of diphenylbenzylamidine hydrochloride (0.52 gram), which had probably dissolved in the benzene. The ether extract was saturated with hydrogen chloride and filtered from precipitated hydrochlorides. It was not found possible to work up the precipitate any further. The ethereal filtrate, on evaporation and crystallisation from alcohol, yielded a very small quantity of benzanilide (m. p. $161-162^{\circ}$ and not depressing the melting point of an authentic specimen).

The Interaction of Benzanilideiminochloride and Phenol at $150-160^{\circ}$.—A mixture of benzanilideiminochloride (6.5 grams) and phenol (3 grams) was heated at $150-160^{\circ}$ in a slow current of carbon dioxide. Fusion to a clear melt took place and hydrogen chloride was evolved. After two hours' heating, the melt was cooled and worked up in the same way as the heated imino-ether hydrochloride, when it gave an identical series of products in similar yields.

N-p-Tolylbenziminophenyl Ether Hydrochloride.—Dry hydrogen

chloride was passed through a solution of *N-p*-tolylbenziminophenyl ether (15 grams) in cold benzene (200 c.c.). The hydrochloride was precipitated from solution by dry ether (500 c.c.) as a viscous oil which rapidly crystallised. When completely crystalline, it was dried in a vacuum desiccator over sulphuric acid and solid sodium hydroxide (yield 15 grams). The hydrochloride is a pale yellow, crystalline solid melting at 132–134° with decomposition (Found: HCl = 11.37. $C_{20}H_{17}ON, HCl$ requires HCl = 11.27 per cent.).

Separation of the Products of Heating N-p-Tolylbenziminophenyl Ether Hydrochloride.—*N-p*-Tolylbenziminophenyl ether hydrochloride (6 grams) was heated for one hour and a half at 160–170° in a slow current of carbon dioxide. The products were worked up in the same way as those from *N*-phenylbenziminophenyl ether, and were found to be (in two separate experiments) free imino-ether (1.72 grams and 1.11 grams), di-*p*-tolylbenzenylamidine hydrochloride (0.2 gram and 0.77 gram), and benzo-*p*-toluidide (0.25 gram and 0.10 gram).

Distillation of N-Phenylbenziminophenyl Ether Hydrochloride in a Current of Hydrogen Chloride.—Dry hydrogen chloride was led through a large bottle to minimise pressure changes, and thence by means of a capillary tube into a Claisen flask containing the heated imino-ether hydrochloride (8 grams). During the first stage of the distillation, heating was effected by an oil-bath gradually raised from 160° to 200°. For subsequent fractions, a naked flame was employed.

Fraction 1 (1.6 grams, b. p. 66–87°, 32 mm.) was a viscous, pale brown oil smelling strongly of phenol. It was extracted with aqueous sodium hydroxide and filtered. The filtrate, shaken with excess of benzoyl chloride, yielded phenyl benzoate (1.98 grams; m. p. 65–68°; melted at 68–69° on crystallisation from alcohol). The residue insoluble in sodium hydroxide was slightly impure iminoether (0.85 gram; m. p. 95–97°; melted at 105° on crystallisation from alcohol).

Fraction 2 (1.2 grams, b. p. 87–215°, 42 mm.) consisted of very sticky, yellow plates. On treatment with hot water, it fused and then set to a white solid (0.8 gram, m. p. 140–150°) which on crystallisation from alcohol yielded benzanilide (0.42 gram, m. p. 161°).

Fraction 3 (2 grams, b. p. 214–230°, 44 mm., mainly between 214° and 216°) consisted of pale yellow, sticky crystals. It was heated with excess of aniline, extracted with boiling dilute hydrochloric acid, and the extract made alkaline with sodium hydroxide. The precipitate (2.43 grams, m. p. 140°) yielded pure diphenyl-

benzenylamidine (1.31 grams, m. p. 146–147°) on crystallisation from alcohol.

Fraction 4 (1.5 grams, b. p. 230–240°/42 mm.) consisted of brownish-yellow crystals. Attempts to separate the constituents of this fraction met with no success.

In a duplicate experiment, fraction 2 was treated with aniline, yielding diphenylbenzenylamidine, and fraction 3 with water, yielding benzanilide, thus showing that these fractions each gave both derivatives characteristic of the imino-chloride.

The author wishes to acknowledge his indebtedness to Dr. J. Kenner for the suggestion of the mechanism of the decomposition.

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[Received, March 12th, 1923.]

CXXXI.—*The Action of Hypochlorous Acid on Bornylene.*

By GEORGE GERALD HENDERSON and JOHN ALEXANDER MAIR.

THE work described in this paper was undertaken with the object of comparing the behaviour of bornylene towards hypochlorous acid with that of camphene, and further of ascertaining if the chlorohydrin, which presumably would be produced, was a chloroborneol or a chloroepiborneol, or possibly a mixture of both.

It has been shown in a former communication (Henderson, Heibron, and Howie, T., 1914, 105, 1367) that dilute aqueous hypochlorous acid converts camphene practically quantitatively into a crystalline chlorohydrin, m. p. 93°, which when heated with zinc and alcohol yields isoborneol, and therefore is a chloroisoborneol. Oxidation with chromic anhydride converts the chlorohydrin into a chloro-ketone, m. p. 132°, from which camphor is obtained on treatment with zinc and alcohol, and which consequently must be a chlorocamphor, possibly β -chlorocamphor. The action of hypochlorous acid on bornylene has been found less simple than on camphene, for although bornylene chlorohydrin is formed, that is not the sole product. On the contrary, the solid obtained as a result of the reaction is a mixture of, at any rate, three different compounds. The separation of the constituents of this mixture was very troublesome, but ultimately we succeeded in isolating two of them—bornylene chlorohydrin and a chlorocamphane—in a fairly pure state.

Bornylene chlorohydrin, $C_{10}H_{17}Cl \cdot OH$, is a soft, crystalline solid,

m. p. 99—101°, which yields a crystalline *p*-nitrobenzoate, m. p. 152°. When heated with zinc and alcohol, it is converted into borneol, which was identified by determination of its melting point and of that of its *p*-nitrobenzoate. Hence the chlorohydrin is shown to be a chloroborneol.

When oxidised with chromic anhydride, bornylene chlorohydrin yields a chloro-ketone, which was found to be identical with the chlorocamphor produced by the oxidation of camphene chlorohydrin (chloroisoborneol). This result was to be expected, because both borneol and isoborneol yield camphor on oxidation.

Camphene chlorohydrin yields isocamphenilanaldehyde when heated with alcoholic potassium hydroxide, or with moist silver oxide in presence of ether, but the action of these reagents on bornylene chlorohydrin takes a different course. Instead of an aldehyde, a compound is formed which reacts with *p*-nitrobenzoyl chloride to give a crystalline *di-p*-nitrobenzoate, m. p. 103—105°, and presumably is a glycol, $C_{10}H_{16}(OH)_2$. Unfortunately, the quantity obtained was so small that we could do little more than prepare the nitrobenzoate of this compound.

It appeared not impossible that an isomeric chlorohydrin—a chloroepiborneol—might also have been formed by the addition of hypochlorous acid to bornylene, but we did not succeed in isolating any such compound from the products of the reaction.

One of the other chloro-compounds which are produced along with bornylene chlorohydrin by the method described is a crystalline solid which has the composition $C_{10}H_{17}Cl$. It is a fully saturated compound, and as it yields camphene when heated with zinc and alcohol it must be a *chlorocamphane*. The purification of this substance being very difficult, it is probable that our specimen still contained a little of a more highly chlorinated compound, and therefore the melting point observed, 71—73°, is probably not that of the pure compound.

Determination of chlorine in the residual product from which the chlorohydrin and the chlorocamphane had been separated indicated the presence of a third compound containing a higher percentage of chlorine. This substance was not isolated in the pure state, but at the same time a specimen which still contained some chlorocamphane was also found to be converted into camphene when heated with zinc and alcohol. Taking this fact, as well as the results of analysis, into account, it seems probable that a dichlorocamphane, $C_{10}H_{16}Cl_2$, was present.

These results are somewhat similar to those obtained by Slawinski (*Bull. Acad. Sci. Cracov*, 1905, 491), who separated from the product of the action of hypochlorous acid on camphene, not only

camphene chlorohydrin, but also a solid camphene dichloride and a mixture of three liquid chlorocamphenes.

EXPERIMENTAL.

Preparation of Bornylene Chlorohydrin.—A solution of 100 grams of bornylene in a little light petroleum was agitated with a dilute aqueous solution of hypochlorous acid in a large stoppered bottle until absorption of the acid was complete. The reaction proceeded rapidly at first, the odour of the acid disappearing almost at once, and after leaving the mixture to stand for a time the aqueous layer was syphoned off, and the bornylene solution shaken with a fresh quantity of the solution of the acid. After several repetitions of this treatment, the product became denser, and it was necessary to add some more light petroleum in order to prevent the formation of an emulsion which separated into two layers very slowly indeed. Finally, the solution of the product was collected, washed with a little water, dried over anhydrous sodium sulphate, and distilled. Each quantity of the aqueous solution withdrawn from the bottle was saturated with common salt and thoroughly extracted with ether, and the residue left on distillation of the ethereal solution was added to the main portion. The crude product was freed from a small quantity of oily and resinous admixtures by distillation in steam, and after several repetitions of the process was obtained in the form of a soft, colourless, crystalline mass, which melted at about 75° . Determinations of the melting point of different fractions, and of the percentage of chlorine contained in them, indicated that the product was not an individual substance but a mixture of the chlorohydrin with at least one, and probably two, other compounds. Fractional distillation in a current of steam effected only a very incomplete separation of these constituents, and their extreme solubility in the usual organic solvents rendered it difficult to isolate them by fractional crystallisation. Ultimately, the chlorohydrin was obtained in a fairly pure condition by preparing a saturated solution of the product in methyl alcohol at the ordinary temperature, leaving the solution to stand in the ice-chest for some time, and quickly collecting by the aid of the pump the crop of crystals which had been deposited. A considerable number of crystallisations carried out in this way gave a substance which melted at $99-101^{\circ}$, and as further crystallisation had little or no effect in raising the melting point, this was considered to be the practically pure chlorohydrin (Found: Cl = 18.5. $C_{10}H_{17}OCl$ requires Cl = 18.8 per cent.).

Bornylene chlorohydrin, $C_{10}H_{16}Cl \cdot OH$, is a soft, colourless, crystalline solid, m. p. $99-101^{\circ}$, with a slight odour resembling that of

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borneol. It is very sparingly soluble in water, but extremely easily soluble in organic solvents, and volatilises very readily in a current of steam. When heated in air, it undergoes partial decomposition.

The *p*-nitrobenzoate was prepared by addition of the calculated quantity of *p*-nitrobenzoyl chloride to a solution of the chlorohydrin in ten times its weight of pyridine. A crystalline product quickly appeared, and after some hours was collected, washed with very dilute sulphuric acid, agitated with dilute aqueous sodium carbonate, and crystallised from alcohol. From this solvent it separates in colourless, lustrous leaflets, which melt at 152° . It is readily soluble in ether or in hot alcohol, and less soluble in benzene or light petroleum (Found : Cl = 10.3; N = 4.2. $C_{17}H_{20}O_4NCl$ requires Cl = 10.5; N = 4.1 per cent.).

Preparation of Bornacol from Bornylene Chlorohydrin.—A 10 per cent. solution of bornylene chlorohydrin in methyl alcohol was heated under reflux with zinc dust until the slow reaction had come to an end. The solution was filtered, the residue washed with methyl alcohol, and the filtrate and washings were mixed with water. The oily liquid which separated was extracted with ether, the ethereal solution washed with water and dried over anhydrous sodium sulphate, the ether removed, and the residue distilled in a current of steam. The solid thus obtained was converted into a *p*-nitrobenzoate by the method described above, and this compound, after purification by crystallisation from alcohol, was found to have the same melting point, namely, 137° , as the *p*-nitrobenzoate of borneol. Moreover, on hydrolysis with alcoholic potassium hydroxide, it yielded a crystalline alcohol of m. p. $207-208^{\circ}$, which undoubtedly was borneol. It is therefore evident that "bornylene chlorohydrin" is a chloroborneol, whilst, on the other hand, it has been shown that "camphene chlorohydrin" is a chloroisoborneol.

Oxidation of Bornylene Chlorohydrin.—The chlorohydrin was oxidised by means of chromic anhydride in glacial acetic acid solution. Oxidation took place fairly readily, and was completed by warming the solution on the water-bath. The oxidation product was then precipitated by addition of water, collected, and distilled in steam, and the solid distillate was converted into a semicarbazone in the usual manner. The semicarbazone crystallised from alcohol in colourless leaflets and was found to have the melting point 223° , practically the same as that of the semicarbazone of the ketone obtained by oxidising camphene chlorohydrin in a similar manner (Found : Cl = 14.5; N = 17.4. $C_{11}H_{18}ON_3Cl$ requires Cl = 14.6; N = 17.3 per cent.). The semicarbazone was decomposed by

heating with the calculated quantity of aqueous oxalic acid, and the liberated ketone was distilled in a current of steam, collected, and purified by crystallisation from methyl alcohol. The chloro-ketone thus produced, $C_{10}H_{15}OCl$, crystallises in small, colourless prisms, m. p. 131—132°. It has only a faint odour, is very easily soluble in organic solvents, and is readily volatilised in steam. From these results it is evident that this chloro-ketone is identical with that obtained by the oxidation of camphene chlorohydrin, being in all probability β -chlorocamphor.

Action of Potassium Hydroxide on Bornylene Chlorohydrin.—

The chlorohydrin was heated under reflux with a methyl alcoholic solution of potassium hydroxide until no further separation of potassium chloride took place, and the solution was then diluted with water and extracted with ether. The ethereal solution was washed with water and dried over anhydrous sodium sulphate, and, after removal of the ether, a viscous liquid was obtained. As camphene chlorohydrin had been found to yield an aldehyde under similar treatment, part of the product from bornylene chlorohydrin was tested with semicarbazide hydrochloride and potassium acetate, but no trace of a semicarbazone was formed. To another part, in solution in pyridine, *p*-nitrobenzoyl chloride was added, in the proportion of 2 mols. of the reagent to 1 mol. of the product, and the liquid was heated on the water-bath for some time. On cooling, a crystalline solid separated, which, after successive washings with dilute sulphuric acid, water, and dilute aqueous sodium carbonate, was recrystallised from alcohol. Owing to the presence of a considerable amount of resinous matter, it was difficult to purify this substance, the final yield being very poor. A little of the compound was ultimately obtained in the form of a crystalline, colourless solid, m. p. 103—105°. From the results of analysis it appeared to be the *di-p-nitrobenzoate* of a glycol of the formula $C_{10}H_{16}(OH)_2$ [Found: N = 6.2. $(NO_2 \cdot C_6H_4 \cdot CO_2)_2 C_{10}H_{16}$ requires N = 6.0 per cent.].

Another portion of the chlorohydrin in ethereal solution was heated for some time under reflux with a slight excess of moist silver oxide. As no silver chloride appeared after several days' heating, the ether was distilled off and replaced by ethyl alcohol containing a little water. The reaction now proceeded with greater rapidity, and when it was completed the product was separated by addition of water and extraction with ether, and then converted into a *p*-nitrobenzoate. This was proved to be identical with the *di-p-nitrobenzoate* of the compound obtained by the action of alcoholic potassium hydroxide on the chlorohydrin. The total quantity of *p*-nitrobenzoate produced was very small, and conse-

quently we were unable to separate and examine the presumed glycol.

Separation of other Chloro-compounds from the Original Product.

As already stated, the product of the action of hypochlorous acid on bornylene contains other chloro-compounds in addition to the chlorohydrin. Partial separation of the chlorohydrin was effected by cooling a solution of the product in methyl alcohol, saturated at the ordinary temperature, and from the residual mixture the other chloro-compounds were obtained as follows. The mixture was dissolved in pyridine and sufficient *p*-nitrobenzoyl chloride added to convert all the chlorohydrin present into the *p*-nitrobenzoate. After the bulk of this ester had crystallised out, the solution was decanted and cautiously neutralised with ice-cold dilute sulphuric acid. The solid which separated was partly purified by distillation in a current of steam and finally crystallised from methyl alcohol by preparing a saturated solution at the ordinary temperature, cooling in the ice chest, and quickly collecting the crystals which had been formed. After several repetitions of this treatment, a fraction was obtained which melted at 71–73°. This fraction was composed of colourless crystals, which have a slight odour reminiscent of that of camphor, are extremely easily soluble in the usual organic solvents, and volatilise readily in steam. The results of analysis pointed to the formula $C_{10}H_{17}Cl$ (Found: Cl = 20.8. Calc., Cl = 20.6 per cent.). The compound is not readily attacked by alcoholic potassium hydroxide, and towards bromine and potassium permanganate behaves as a saturated substance. Hence we concluded that it must be a chloro-camphane. This view was confirmed by heating it under reflux with zinc dust and alcohol until the reaction was complete, when the product, after purification by steam distillation and crystallisation from alcohol, was found to be a saturated hydrocarbon of m. p. 153°, which undoubtedly was camphane.

The quantity of this chloro-camphane in our hands was too small to permit of complete purification, and our specimen certainly contained a small proportion of a more highly chlorinated substance. Hence the melting point observed cannot be regarded as that of the pure chloro-camphane.

The more soluble part, from which this compound had been separated, was not further purified, owing to lack of material, but analysis showed the probable presence of a dichloro-camphane mixed with some of the monochloro-camphane. Thus one fraction was found to contain 29.9 per cent. of chlorine, whilst $C_{10}H_{16}Cl_2$ requires Cl = 34.3 per cent. Moreover, this more soluble portion was also found to yield camphane on treatment with zinc dust

and alcohol. Hence it may be concluded that a chlorocamphane and a dichlorocamphane, $C_{10}H_{16}Cl_2$, are formed in addition to the chlorohydrin by the action of hypochlorous acid on bornylene.

We are indebted to the Department of Scientific and Industrial Research for enabling one of us (J. A. M.) to take part in this work, and to the Carnegie Trust for a grant which defrayed some of the expense.

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[Received, March 29th, 1923.]

(XXXII).—*Organo-derivatives of Thallium. Part VI.* *Compounds of the Type R_2TlX .*

By ARCHIBALD EDWIN GODDARD.

It has recently been shown (Goddard, T., 1922, **121**, 36) that the thalliumdialkyl salts prepared from the acids of the fatty series from formic to *n*-octoic exhibit a fall of melting point with increasing molecular weight, this probably being connected with decrease of ionisation in the case of the higher members. These salts are now compared with the corresponding phenyl compounds, which were prepared by the interaction of thalliumdiphenyl bromide, silver oxide, and the fatty acid in xylene solution. The following salts were isolated: acid *thalliumdiphenyl propionate*, m. p. 164° ; the acid *butyrate*, m. p. 171° ; the normal *butyrate*, m. p. 230° ; the acid *valerate*, m. p. 176° ; the acid *n-hexanoate*, m. p. 191° ; the normal *hexanoate*, m. p. 208° ; and the *n-octanoate*, m. p. 195° . It will be noted that whilst the melting points of the acid salts rise as the series is ascended, those of the normal derivatives fall, just as in the case of the dialkyl salts. Whilst the solubility of the latter salts, however, increases as the molecular weight increases, the thalliumdiphenyl salts have a markedly decreased solubility in organic media.

Thalliumdiphenyl o- and m-bromobenzoates and the *p-nitrobenzoate* were prepared from the corresponding substituted benzoic acids by the above method. Of the former two, the meta-derivative is the less soluble; the nitrobenzoate is more insoluble than the corresponding thalliumdiethyl salt.

It was pointed out (Goddard, T., 1921, **119**, 1310) that thalliumdialkyl hydroxides react with the hydroxyl groups in nitro-substituted phenols. This observation has now been extended to include nitronaphthols and nitroso-compounds, and by the aid of thalliumdiphenyl oxide, phenyl compounds of the same type have been isolated.

By the interaction of thalliumdiethyl hydroxide and hexanitrodiphenylamine, *thalliumdiethyl hexanitrodiphenylamine* was obtained in brilliant crimson plates, the colour being much more intense than that of the ammonium salt (*aurantia*). *Thalliumdiethyl p-benzoquinoneoximate* was isolated as the quinhydrone, that is, containing one molecule of nitrosophenol of crystallisation, and in agreement with the rule that quinhydrone formation intensifies colour, this compound is blue black. In the case of *thalliumdiethyl* and *thalliumdiphenyl 1:2-naphthaquinone-1-oximates*, however, the green colour, which is similar to that of the alkali salts, indicates conclusively that complex formation involving the nitroso-group does not occur.

Thalliumdiethyl 2:6-dinitrophenoxide has a greater solubility, and is of a deeper orange colour, than the 2:4-derivative previously described, the latter difference being in agreement with the observation that those compounds of this type having the nitro- and hydroxyl-groups closer together display more intense colour. *Thalliumdiethyl dinitro-o-tolylxide*, which is the most explosive of the compounds now described, crystallises in deep orange plates; the *thalliumdiethyl* and *thalliumdiphenyl trinitro-m-tolylxides* are deposited in brilliant yellow needles, whereas the picrates are decidedly orange.

Three naphthoxides have been isolated, namely, *thalliumdiethyl* and *thalliumdiphenyl trinitro- α -naphthoxides*, the former being deep yellow and the latter pale orange, and *thalliumdiethyl dinitro- β -naphthoxide*, which is dull yellow. The analogue of "naphthol yellow S," *thalliumdiethyl 2:4-dinitronaphthoxide-7-sulphonate*, was isolated in long, golden-yellow needles.

Thalliumdiphenyl o- and p-nitrophenoxides are paler in colour than the thallium-dimethyl and -diethyl derivatives and are much less soluble in the usual solvents.

In several previous communications the interaction of thallic chloride and various organo-metallic compounds was studied; the investigation has now been extended with the idea of drawing some definite conclusions from the results of these reactions. Since mercury derivatives have been of considerable value in the production of organo-compounds containing metals, a more detailed investigation of their properties has been made. Mercury dipropyl, now prepared for the first time by the Grignard reaction, yields with thallic chloride, thallous chloride, mercury propyl chloride, and thalliumdipropyl chloride. Mercury diisobutyl, on the other hand, only gives thallous chloride and mercury isobutyl chloride. It was shown (Goddard, T., 1922, 121, 40) that mercury diphenyl and thallic chloride gave rise to thalliumdiphenyl chloride, but it

is now found that mercury dibenzyl yields thallous chloride, mercury benzyl chloride, and traces of dibenzyl, a decided resemblance between the *iso*amyl and benzyl radicles being thus indicated. With the hope of preparing mixed thallium compounds, thallic chloride was treated with mercury benzyl ethyl in ethereal solution, but mercury ethyl chloride, mercury benzyl chloride, and thallous chloride resulted, the odour of benzaldehyde also being noted. Whilst 2-chloromercurithiophen and mercury 2 : 2'-dithienyl readily react with arsenic trichloride to form organo-derivatives (Steinkopf and Baucrmeister, *Annalen*, 1917, **413**, 331), thallic chloride causes the decomposition of the first compound only, the second giving no organic thallium compound. Better results are not obtained when thallic chloride and thiophen are heated together in the presence of mercuric chloride, but 2-iodomercurithiophen, treated as above, yields 2-chloromercurithiophen and thallous chloride.

When thallic chloride in ethereal solution and *p*-aminophenyl mercuriacetate are shaken together, an unstable additive compound seems to be formed. It contains 11.06 per cent. of chlorine and 19.51 per cent. of thallium, corresponding to the formula $2C_6H_5O_2NHg_2TlCl_3$; *p*-aminophenyl mercurichloride behaves similarly, but if the above solutions are heated complete decomposition will take place. Neither *p*-bismercurianiline nor sodiocamphor gives rise to organic thallium compounds. It can be concluded from the above that only normal compounds of the type R_2Hg give rise to thallium derivatives where R is any radicle except benzyl, thienyl, or an *iso*-group; in other cases substances of the type R_2TlX are produced.

It was recently shown (Goddard, *loc. cit.*) that thallic chloride and triphenylstibine yield thallous chloride and triphenylstibine dichloride, and it is now found that the latter compound, after being heated with thallic chloride in xylene solution and kept for several months, gives thallous chloride and metallic antimony. *Tri-p-xylylstibine* reacts like the phenyl compound, yielding *tri-p-xylylstibine dichloride*. In order to find out if the reaction between thallic chloride and an aromatic arsine is a general one, *tri-m-* and *tri-p-xylylarsines*, prepared by the Grignard reaction, were examined and found to yield the corresponding xylylarsenious chlorides. The reaction in the case of compounds of the elements in Group V can be summarised by stating that phosphorus and antimony yield no organo-thallium derivatives, whereas arsenic and bismuth are capable of yielding compounds of the type R_2TlX .

Tin triethyl chloride reacts with thallic chloride with production of tin diethyl chloride, whilst tin diethyl iodide interacts according to the equation $Et_2SnI + TlCl_3 = Et_2SnCl_2 + Tl + I + ICl$. Tin

dimethyl diethyl yields thallous chloride, thalliumdiethyl chloride, and tin dimethyl chloride.

In the aromatic series, an attempt was made to prepare lead tetra-*m*-xylyl in order to have an easy method of obtaining the unknown thalliumdixylyl chloride, but *lead tri-m-xylyl* was isolated, even when the quantities used in the Grignard reaction should have given the tetraxylyl derivative. The compound thus obtained was monomolecular, although in more concentrated solutions it would no doubt associate. The investigation of this compound was not continued owing to the work of Krause in this field. It reacts, however, with thallie chloride to yield *lead di-m-xylyl dichloride* and thallous chloride.

Summarising the work carried out on compounds of tin and lead in the aromatic and aliphatic series, substances of the type R_2M give rise to R_2MX_2 and R_2TlX : R_3MX and R_3MR' yield thallous chloride and R_2MX_2 and R_3MX , respectively; $R_3MR'_2$ produces R'_2MX_2 and R'_2TlX , where R' is the radicle of lower molecular weight; and R_2MX_2 merely exchanges its halogen, X_2 , should it be bromine or iodine, for the chlorine of the thallie chloride.

Thalliumdiphenyl chloride is broken down by iodine monochloride as follows: $Ph_2TlCl + 2ICl = 2PhCl + TlCl + I_2$. This differs from the reaction with thalliumdiethyl bromide, where only thallous iodide was isolated.

EXPERIMENTAL.

The following derivatives of thalliumdiphenyl hydroxide were prepared.

Acid Propionate.—A mixture of 1 gram of thalliumdiphenyl bromide, 0.265 gram of silver oxide, and 0.63 gram of propionic acid (4 mol.) in 30 c.c. of toluene was boiled for two hours. Most of the solid dissolved and filtering and concentration yielded 0.5 gram of transparent, silky needles, which after washing with light petroleum melted at 164° (Found: $Tl = 40.31$. $C_{18}H_{21}O_4Tl$ requires $Tl = 40.38$ per cent.). The acid salt is readily soluble in cold chloroform, hot alcohol, pyridine, ethyl acetate, or glacial acetic acid, fairly soluble in boiling water, and insoluble in ether or light petroleum.

Acid Valerate.—Using the above quantities and 0.48 gram of valeric acid (2 mol.), 0.55 gram of fine, white needles were obtained, m. p. 176° (Found: $Tl = 36.19$, 36.81 . $C_{22}H_{29}O_4Tl$ requires $Tl = 36.35$ per cent.). The salt is readily soluble in cold pyridine, alcohol, acetone, chloroform, or ether and in warm carbon tetrachloride or water, and insoluble in light petroleum or cold water.

This salt may be recrystallised from chloroform without removing the acid of crystallisation.

Acid Butyrate.—In this case, 0.30 gram ($1\frac{1}{2}$ mols.) of butyric acid was used and 0.5 gram of waxy needles was isolated, m. p. 171° (Found: $Tl = 38.24$. $C_{20}H_{25}O_4Tl$ requires $Tl = 38.26$ per cent.). The salt, which is soluble in all the solvents except light petroleum, was dissolved in acetone and reprecipitated with light petroleum, when the acid of crystallisation was removed, and the normal salt obtained, m. p. 230° (Found: $Tl = 45.65$. $C_{16}H_{17}O_2Tl$ requires $Tl = 45.83$ per cent.).

Acid Hexoate.—Using 0.5 gram of *n*-hexoic acid, 0.55 gram of feathery rosettes of needles was obtained, m. p. 191° (Found: $Tl = 34.66$. $C_{24}H_{33}O_4Tl$ requires $Tl = 34.62$ per cent.). By treating this acid salt as was the acid butyrate, the normal *n*-hexoate was obtained, m. p. 208° .

n-Octoate.—Prepared by using 0.3 gram (1 mol.) of *n*-octoic acid, when 0.6 gram of waxy needles, m. p. 195° , was obtained (Found: $Tl = 40.07$. $C_{28}H_{37}O_4Tl$ requires $Tl = 40.70$ per cent.). The salt is the least soluble of the series.

p-Nitrobenzoate.—One gram of thalliumdiphenyl bromide, 0.294 gram of silver oxide, and 0.356 gram of *p*-nitrobenzoic acid in 40 c.c. of toluene were boiled for five hours. From the mixture, 0.5 gram of faintly yellow, blunt-ended needles was isolated, which, after washing with light petroleum, melted at 228° (Found: $Tl = 38.35$; $N = 2.69$. $C_{19}H_{11}O_4NTl$ requires $Tl = 38.92$; $N = 2.67$ per cent.). The salt is soluble in cold pyridine, hot acetone, toluene, or ethyl acetate, and insoluble in chloroform, carbon tetrachloride, or light petroleum.

o-Bromobenzoate.—Prepared from 1.24 grams of thalliumdiphenyl bromide, 0.33 gram of silver oxide, and 0.576 gram of *o*-bromobenzoic acid, by boiling in toluene for one and a half hours, 0.1 gram of glistening, cream plates were isolated (Found: $Br = 14.82$. $C_{19}H_{13}O_2BrTl$ requires $Br = 14.32$ per cent.). Free acid was removed by washing with ether, the compound then melting at 243° . It is soluble in organic solvents with the exception of ether and light petroleum.

m-Bromobenzoate.—Using the above quantities, 0.2 gram of glistening plates were obtained, m. p. 247° (Found: $Br = 14.49$. $C_{19}H_{13}O_2BrTl$ requires $Br = 14.32$ per cent.). The salt is soluble in pyridine or toluene, fairly soluble in ethyl acetate, slightly soluble in acetone, and insoluble in other organic solvents.

o-Nitrophenoxide.—Thalliumdiphenyl oxide (0.56 gram) and 0.278 gram of *o*-nitrophenol were mixed in a few drops of alcohol, 50 c.c. of water added, and the whole was boiled for half an hour, cooled,

and filtered. The residue was washed with alcohol, then agitated with ether to remove free nitrophenol, when 0.579 gram of a bright orange, crystalline powder was isolated. It melted at 247° to a blood-red liquid, and when gently heated turned scarlet, reverting to its original colour on cooling (Found: $\text{Tl} = 41.64$; $\text{N} = 2.52$, $\text{C}_{18}\text{H}_{14}\text{O}_3\text{NTl}$ requires $\text{Tl} = 41.12$; $\text{N} = 2.82$ per cent.). The salt is soluble in cold pyridine, fairly soluble in acetone or alcohol, giving yellow solutions, slightly soluble in toluene (becoming scarlet), ether or hot water, and insoluble in carbon tetrachloride or ethyl acetate, becoming decolorised in the latter.

p-Nitrophenoxide.—From a mixture of 1.05 grams of thalliumdiphenyl chloride, 0.5 gram of silver oxide ($\frac{1}{2}$ mol. excess), and 0.4 gram of *p*-nitrophenol in 60 c.c. of water, by boiling for three hours, a lemon-yellow product was obtained. After boiling this with 250 c.c. of water, filtering hot, and concentrating, 0.2 gram of bright yellow needles was isolated, which, after washing with alcohol and ether, melted at 251° with evolution of gas (Found: $\text{Tl} = 41.19$. $\text{C}_{18}\text{H}_{14}\text{O}_3\text{Tl}$ requires $\text{Tl} = 41.12$ per cent.). The salt differs from the ortho-compound by being slightly soluble in ethyl acetate and insoluble in alcohol, ether, or chloroform.

1:2-Naphthaquinone-1-oximate.—A mixture of 0.40 gram of thalliumdiphenyl oxide and 0.148 gram of α -nitroso- β -naphthol in 50 c.c. of water, after boiling for three hours, was kept overnight, when an insoluble, green powder was obtained (Found: $\text{Tl} = 40.23$. $\text{C}_{20}\text{H}_{16}\text{O}_2\text{NTl}$ requires $\text{Tl} = 40.31$ per cent.). The compound crystallised from ether in microscopic, green needles, m. p. 238° . It differs from the corresponding diethyl compound (below) in its insolubility in water and in that most of its solutions are green.

Trinitro-m-tolylxide.—From 0.5 gram of thalliumdiphenyl oxide and 0.332 gram of trinitro-*m*-cresol, 0.4 gram of yellow needles was obtained, m. p. 231° (Found: $\text{Tl} = 33.96$; $\text{N} = 6.81$. $\text{C}_{19}\text{H}_{14}\text{O}_7\text{N}_3\text{Tl}$ requires $\text{Tl} = 33.99$; $\text{N} = 7.00$ per cent.). The salt is soluble to some degree in most organic solvents and gives an orange solution in toluene.

Trinitro- α -naphthoride.—From 0.5 gram of thalliumdiphenyl oxide and 0.381 gram of trinitro- α -naphthol, 0.53 gram of brilliant orange needles was isolated, which melted to a blood-red liquid at 232° (Found: $\text{Tl} = 32.01$; $\text{N} = 6.59$. $\text{C}_{22}\text{H}_{14}\text{O}_7\text{N}_3\text{Tl}$ requires $\text{Tl} = 32.07$; $\text{N} = 6.61$ per cent.). The salt is similar in solubility to the ethyl compound (below).

The following derivatives of thalliumdiethyl hydroxide were prepared.

Thalliumdiethyl Hexanitrodiphenylamine.—The thalliumdiethyl

hydroxide derived from 1.52 grams of the corresponding bromide was treated with 1.9 grams of hexanitrodiphenylamine in 50 c.c. of water and boiled for fifteen minutes. After three crystallisations from water, 1.1 grams of brilliant carmine plates having a violet reflex were obtained, m. p. 224° to a blood-red liquid (Found: $Tl = 29.14$; $N = 13.50$. $C_{16}H_{14}O_{12}N_7Tl$ requires $Tl = 29.14$; $N = 14.01$ per cent.). The compound is insoluble in toluene, light petroleum, or chloroform and soluble in other organic media.

p-Benzoquinoneoximate.—The hydroxide from 0.5 gram of thallium-diethyl bromide was treated with 0.18 gram of *p*-nitrosophenol, and 0.4 gram of blue-black needles having a violet reflex was isolated (Found: $Tl = 40.57$; $N = 5.58$. $C_{10}H_{11}O_2NTl, C_6H_5O_2N$ requires $Tl = 40.22$; $N = 5.53$ per cent.). The oximate is soluble in water or pyridine, slightly soluble in alcohol, giving a brown solution, and insoluble in other organic solvents.

1:2-Naphthaquinone-1-oximate.—Treating twice the above quantity of hydroxide with 0.46 gram of α -nitroso-3-naphthol, 0.7 gram of deep green product was obtained (Found: $Tl = 46.55$; $N = 3.21$. $C_{12}H_{16}O_2NTl$ requires $Tl = 46.99$; $N = 3.23$ per cent.). The salt crystallises from alcohol in deep green needles, m. p. 217° , is insoluble in light petroleum, and readily soluble in other organic solvents, the solutions being coloured brown, with the exception of alcohol and carbon tetrachloride, which give green solutions.

2:6-Dinitrophenoxide.—Thalliumdiethyl hydroxide (0.5 gram) and 0.27 gram of 2:6-dinitrophenol gave 0.35 gram of deep orange plates, which sintered at 182° and melted with decomposition at 190° (Found: $N = 6.33$. $C_{10}H_{13}O_5N_2Tl$ requires $N = 6.29$ per cent.). The salt is soluble in the usual solvents with the exception of light petroleum, and the solutions are yellow in colour.

Dinitro-*o*-tolylxide.—The above amount of hydroxide and 0.29 gram of dinitro-*o*-cresol yielded 0.53 gram of terra-cotta plates, which blackened at 215° and exploded with great violence at 219° (Found: $Tl = 44.62$; $N = 6.05$. $C_{11}H_{13}O_5N_2Tl$ requires $Tl = 44.43$; $N = 6.10$ per cent.). The compound gives a yellow solution in acetone or ethyl acetate, orange in other solvents, and is insoluble in carbon tetrachloride or light petroleum.

Trinitro-*m*-tolylxide.—Using 0.35 gram of trinitro-*m*-cresol, 0.62 gram of brilliant yellow needles was obtained, sintering at 203° and decomposing at 214° (Found: $Tl = 40.33$; $N = 8.32$. $C_{11}H_{14}O_7N_3Tl$ requires $Tl = 40.47$; $N = 8.34$ per cent.). This compound is not so readily attacked by fuming nitric acid as the dinitro-derivative and has a similar solubility.

Trinitro- α -naphthoxide.—The hydroxide from 0.9 gram of thallium-

diethyl bromide with 0.73 gram of trinitro- α -naphthol yielded 0.95 gram of orange plates, sintering at 213° and melting with considerable gas evolution at 220° (Found: $\text{TI} = 37.65$; $\text{N} = 7.85$, $\text{C}_{14}\text{H}_{14}\text{O}_7\text{N}_3\text{TI}$ requires $\text{TI} = 37.77$; $\text{N} = 7.78$ per cent.). The salt is slightly soluble in chloroform or toluene, insoluble in light petroleum, and soluble in other organic media.

Dinitro- β -naphthoxide.—By concentrating the solution from 0.42 gram of thalliumdiethyl hydroxide and 0.68 gram of dinitro- β -naphthol, 0.35 gram of dull greenish-yellow, microscopic, flat-ended blades was deposited. These commenced to decompose at 208° , but, although charring with rise of temperature, did not actually melt at 280° (Found: $\text{TI} = 41.09$, $\text{C}_{11}\text{H}_{15}\text{O}_5\text{N}_2\text{TI}$ requires $\text{TI} = 41.20$ per cent.). The salt is soluble in pyridine or acetone, moderately soluble in alcohol, giving a reddish-yellow solution, slightly soluble in chloroform, ethyl acetate, or ether, becoming bright yellow in the last, and insoluble in carbon tetrachloride, toluene, or light petroleum.

2:4-Dinitronaphthoxide-7-sulphonate.—By treating 0.42 gram of thalliumdiethyl hydroxide with 0.23 gram of 2:4-dinitronaphthol-7-sulphonic acid, 0.4 gram of pale orange needles was obtained, which darkened at 217° , but did not melt at 280° (Found: $\text{TI} = 46.47$; $\text{N} = 3.27$, $\text{C}_{18}\text{H}_{21}\text{O}_8\text{N}_2\text{STI} \cdot 2\text{H}_2\text{O}$ requires $\text{TI} = 46.77$; $\text{N} = 3.21$ per cent.). The salt is soluble in cold acetone or warm pyridine, moderately soluble in alcohol, and insoluble in other solvents; the color deepens in toluene.

Preparation of Mercury Dipropyl and its Action on Thallie Chloride.—To the solution from 23 grams of *n*-propyl bromide and 4.3 grams of magnesium in 100 c.c. of ether, 24.3 grams of mercuric bromide were added in small portions. The reaction was accompanied by violent boiling and all the mercuric bromide went into solution, after which the mixture was boiled for one hour and then decomposed by water. Extraction with ether yielded 45 grams of mercury propyl bromide and 6.0 grams of mercury dipropyl (b. p. $189-191^{\circ}$). A small quantity of metallic mercury was also obtained.

Thallie chloride (1 mol.) was added to 5.2 grams of mercury dipropyl in 50 c.c. of ether, a vigorous reaction taking place, and 6.9 grams of solid separated after standing over-night. This was washed with ether, which removed mercury propyl chloride; the remaining solid gave 0.85 gram of thallous chloride and 2.2 grams of thalliumdipropyl chloride, after treatment with alcohol (Found: $\text{Cl} = 19.20$. Calc., $\text{Cl} = 19.89$ per cent.).

Interaction of Mercury Diisamyl and Thallie Chloride.—To 5 grams of mercury diisamyl, 4.5 gram of thallie chloride in 25 c.c.

of ether were added and the mixture was boiled for fifteen minutes. After filtering, the residue consisted of 2.0 grams of thallous chloride; the filtrate yielded 2.5 grams of needles, m. p. 86° , identified as mercuric isoamyl chloride.

Interaction of Mercury Dibenzyl and Thallic Chloride.—A solution of mercury dibenzyl (1.1 grams) and 1.1 grams of thallic chloride in 30 c.c. of ether was boiled, kept for several days, and then filtered hot. A residue of 0.75 gram of thallous chloride was obtained, whilst the filtrate yielded 1.2 grams of mercury benzyl chloride (m. p. 104°) and traces of dibenzyl.

Interaction of Mercury Benzyl Ethyl and Thallic Chloride.—The product from the interaction of 20.3 grams of magnesium ethyl bromide and 12 grams of mercury benzyl chloride was treated with excess of thallic chloride in ethereal solution. A white precipitate formed, and after standing a short time, this was filtered off and washed with ether, the remaining solid yielding 2.95 grams of thallous chloride, and the ethereal washings 0.25 gram of mercury ethyl chloride. The main filtrate, on evaporation in a vacuum, gave 7.75 grams of solid, which was boiled with alcohol and filtered. A residue of 0.8 gram of thallous chloride was obtained, the filtrate depositing 2.2 grams of mercury ethyl chloride, m. p. 192° ; further evaporation yielded 0.2 gram of mercury benzyl chloride, m. p. 104 – 105° . Removal of the last traces of alcohol gave 0.5 gram of an oil, having a strong odour of benzaldehyde.

Interaction of 2-Iodo-mercuri-thiophen and Thallic Chloride.—Two grams of 2-iodo-mercuri-thiophen were added to 1.5 grams of thallic chloride in 50 c.c. of absolute alcohol. A yellow coloration developed, and after boiling for fifteen minutes the mixture was filtered hot. The residue (1.1 grams) consisted of thallous chloride, and the partly evaporated filtrate yielded 1.0 gram of 2-chloro-mercuri-thiophen, m. p. 183° . Further evaporation gave a small quantity of crystals which contained iodine.

Interaction of Triphenylstibine Dichloride and Thallic Chloride.—Triphenylstibine dichloride (3.5 grams) and 3 grams of thallic chloride were boiled in 50 c.c. of xylene for two hours. The mixture gradually blackened, and after standing for a week the residue was filtered off; it consisted of thallous chloride (0.9 gram). After six months, during which the filtrate spontaneously evaporated, the residue, consisting of long needles and shining plates, was washed with acetone; the undissolved plates were found to be metallic antimony (0.6 gram). Evaporation of the acetone gave rods an inch in length (0.95 gram) which were unchanged triphenylstibine dichloride, m. p. 143° . Since the filtrate obtained after the removal of the thallous chloride was free from solid matter, the

separation of the antimony must have been due to reduction at the ordinary temperature.

(a) *Preparation of Tri-p-xylylstibine.* (b) *Its Reaction with Thallie Chloride.*—(a) To a solution of 24 grams of bromo-*p*-xylene and 3.5 grams of magnesium in 50 c.c. of ether, 9 grams of antimony trichloride in 20 c.c. of the same solvent were gradually added. The reaction was not very violent and the whole was boiled for four hours, then decomposed with water, and filtered. The residue was dried and boiled with benzene, the solution on evaporation yielding 7.25 grams of short, transparent needles, m. p. 174.5° (Found: Sb = 28.13. $C_{24}H_{27}Sb$ requires Sb = 27.61 per cent.).

Tri-p-xylylstibine is readily soluble in benzene, cold chloroform, or boiling glacial acetic acid, moderately soluble in hot acetone, and less soluble in ether or alcohol.

(b) To a solution of 2.17 grams of tri-*p*-xylylstibine in 30 c.c. of benzene, 1.55 grams of thallie chloride were added and the mixture was kept over-night. After filtration, 1.8 grams of thalious chloride were obtained, and evaporation of the benzene and addition of light petroleum yielded 1.3 grams of substance, which after recrystallisation melted at $230-231^{\circ}$ (Found: Cl = 14.01. $C_{24}H_{27}Cl_2Sb$ requires Cl = 14.01 per cent.).

Tri-p-xylylstibine dichloride is a crystalline powder, soluble in cold chloroform, acetone, or benzene, moderately soluble in pyridine, and insoluble in light petroleum.

Preparation of (a) Tri-p-xylylarsine, (b) Tri-m-xylylarsine.—

(a) To the solution obtained from 3.62 grams of magnesium and 27.9 grams of bromo-*p*-xylene in 50 c.c. of dry ether 9 grams of arsenic trichloride in 30 c.c. of light petroleum were gradually added. The reaction was very violent and a grey-green, gelatinous precipitate separated out, this finally becoming white on standing. After several hours, the mixture was decomposed with water, the whole extracted with ether, the solution, on drying and evaporating, yielding fine, white needles, identical in properties with the compound obtained by Michaelis. Yield 8.5 grams.

(b) This was prepared as above, the yield being 8 grams.

Action of Thallie Chloride on the Preceding Arsines.—To 3.9 grams of tri-*p*-xylylarsine in 40 c.c. of toluene, 3.4 grams of thallie chloride were added. A white precipitate was thrown down, and the whole after boiling for forty minutes was filtered, the residue washed with ether, 1.5 grams of thalious chloride being obtained. Evaporation of the filtrate yielded an oil, which was soluble in acetone, the addition of light petroleum depositing tufts of needles (3.67 grams), m. p. 63° , identified as *p*-xylylarsenious chloride. The

etheral washings yielded 0.3 gram of unchanged arsine. When the reaction was carried out in the cold in benzene, the same products were isolated.

When 2.0 grams of tri-*m*-xylylsarsine and 1.55 grams of thallic chloride were treated as above, 1.0 gram of thalrous chloride and 1.69 grams of *m*-xylylsarsenious chloride, m. p. 44° , were obtained.

Interaction of (a) Tin Triethyl Chloride, (b) Tin Diethyl Iodide, (c) Tin Dimethyl Diethyl and Thallic Chloride.—(a) One gram of tin triethyl chloride in 30 c.c. of ether was added to 1.3 grams of thallic chloride in 3.25 c.c. of the same solvent. A pale yellow precipitate separated out, and after standing one hour the mixture was filtered hot. The residue consisted of thalrous chloride (0.82 gram), and the filtrate yielded, in addition to thallic chloride, a small quantity of tin diethyl chloride.

(b) To a solution of 0.4 gram of thallic chloride in 20 c.c. of ether, 0.5 gram of tin diethyl iodide was added, a black solid being immediately precipitated. After standing for one hour, the mixture was boiled for fifteen minutes and filtered. The residue (0.15 gram) consisted of metallic thallium, mixed with traces of iodine. The filtrate on evaporation deposited white, feathery needles, m. p. 83° , which were identified as tin diethyl chloride, and further evaporation yielded iodine and a small quantity of substance having the properties of iodine monochloride.

(c) When 2.07 grams of tin dimethyl diethyl were added to 3.02 grams of thallic chloride in 15 c.c. of ether, a yellow precipitate was deposited, which was mixed with shining crystals. After boiling for half an hour and filtering, a residue of 1.15 grams was obtained. This consisted of thalrous chloride and thallium diethyl chloride, and evaporation of the filtrate gave 0.7 gram of thallic chloride and a small quantity of crystals of tin dimethyl chloride, m. p. 90° .

*Preparation of Lead Tri-*m*-xylyl and its Action on Thallic Chloride.*—To a solution of 20.55 grams of bromo-*p*-xylene and 3.12 grams of magnesium in 100 c.c. of ether, 11.6 grams of lead chloride were added in small quantities, and the mixture was boiled for five hours. Metallic lead soon commenced to separate out and the colour of the solution changed from brownish-red to green. The mixture was decomposed with water, filtered, and the dry residue extracted with benzene. Evaporation of the solvent gave 2.5 grams of a very pale yellow, crystalline powder (Found: C = 54.97; H = 5.27; Pb = 39.63. $C_{12}H_{10}Pb$ requires C = 55.13; H = 5.21; Pb = 39.66 per cent.). Molecular-weight determinations by the cryoscopic method in benzene (0.746 and

0.548 gram in 14.4868 and 19.5566 grams of benzene, respectively) gave $M = 495$, 519. $C_{24}H_{27}Pb$ requires $M = 522.4$.

Lead tri-m-xylyl, after crystallising from acetone, then three times from benzene, melted sharply at 233.5° with the separation of metallic lead. The compound is soluble in chloroform or toluene, and slightly soluble in acetone, light petroleum, or pyridine. Its solutions precipitate silver oxide from alcoholic silver nitrate.

Lead tri-*m*-xylyl (0.5 gram) in 5 c.c. of benzene was treated with 1 mol. of thallie chloride in 1 c.c. of ether, a precipitate separating, and the solution becoming warm. After standing for a week, lustrous rods in star-like clusters had crystallised out. The filtrate from this product yielded thallie chloride, and the residue was boiled with benzene to remove thallous chloride. Needles were obtained from the benzene (Found: Cl = 14.71. $C_{16}H_{18}Cl_2Pb$ requires Cl = 14.54 per cent.). The compound appears to be slightly more soluble in organic media than lead diphenyl chloride.

Action of Iodic Monochloride on Thalliumdiphenyl Chloride.—To 0.5 gram of thalliumdiphenyl chloride in 4 c.c. of light petroleum, 0.82 gram (2 mols.) of iodic monochloride in 10 c.c. of the same solvent was added, and the whole was boiled for two hours, when nearly all the solid had disappeared. The residue obtained on filtering (0.25 gram) was thallous chloride, and evaporation of the filtrate gave 0.3 gram of iodine.

The author is indebted to the Research Fund Committee of the Chemical Society for a grant which has partly defrayed the expenses of this investigation.

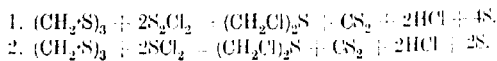
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[Received, March 5th, 1923.]

CXXXIII.—The $\alpha\alpha'$ -Dichlorodialkyl Sulphides.

By FREDERICK GEORGE MANN and WILLIAM JACKSON POPE.

LITTLE has been published concerning the $\alpha\alpha'$ -dichlorodialkyl sulphides, although Riche long ago (*Ann. Chim. Phys.*, 1855, [iii], 43, 283) obtained a dichlorodimethyl sulphide as a yellow, unpleasantly smelling liquid by the chlorination of dimethyl sulphide. Bloch and Höhn have recently shown (*Ber.*, 1922, 55, [B], 53) that sulphur monochloride acts upon trithioformaldehyde with formation of $\alpha\alpha'$ -dichlorodimethyl sulphide in accordance with equation 1:



It is shown in the present paper that the yield is only about 70 per cent. of that indicated by this equation, but that sulphur dichloride acts practically quantitatively upon trithioformaldehyde in accordance with equation 2.

An excellent yield of $\alpha\alpha'$ -dichlorodimethyl ether was obtained by Descudé (*Bull. Soc. chim.*, 1906, [iii], 35, 953) by treating trioxymethylene with phosphorus trichloride in presence of zinc chloride; it was thus suggested that $\alpha\alpha'$ -dichlorodimethyl sulphide might be obtained conveniently by the action of phosphorus trichloride and zinc chloride on trithioformaldehyde. The latter substance is, however, stable towards mixtures of these reagents.

When either of the sulphur chlorides acts upon α -trithioacetaldehyde a mixture of the $\alpha\alpha'$ -dichlorodiethyl sulphide recently described by Bales and Nickelson (*T.*, 1922, 121, 2137) with the previously unknown *diethylidene trisulphide*, $\text{S} \begin{smallmatrix} \text{CHMe} \\ \text{CHMe} \end{smallmatrix} \text{S}_2\text{S}$, results.

Conclusive evidence in favour of the constitution now advanced for the latter substance cannot yet be produced, but the liberation of sulphur when the compound is treated with nitric acid suggests that the constitution is correctly stated. Diethylidene trisulphide, however, behaves curiously towards both methyl iodide and $\alpha\alpha'$ -dichlorodiethyl sulphide, giving with both β -trithioacetaldehyde.

EXPERIMENTAL.

$\alpha\alpha'$ -Dichlorodimethyl Sulphide.—1. *From trithioformaldehyde and sulphur monochloride.* When pure sulphur monochloride, prepared as we have previously described (*T.*, 1921, 119, 636) and in the proportion—1.3 mols.—actually used by Bloch and Höhn, is added to powdered trithioformaldehyde, the vigorous reaction observed by these authors does not occur; on heating in boiling water at 100° , hydrogen chloride is evolved freely and after an hour a red liquid results. On distillation under ordinary pressure, more hydrogen chloride escapes and a liquid comes over up to 140° , followed by a little unchanged trithioformaldehyde; a residue of tarry sulphur remains. The fractional distillation of the product yields carbon disulphide, a liquid boiling at 108 – 109° which is probably a mixture (C = 24.8; H = 5.4; Cl = 28.1; S = 42.1 per cent.), and $\alpha\alpha'$ -dichlorodimethyl sulphide boiling at 155 – 156° . When a larger proportion (2 mols.) of sulphur monochloride is used, the intermediate fraction boiling at 108 – 109° is not obtained, but the $\alpha\alpha'$ -dichlorodimethyl sulphide is contaminated with a little sulphur monochloride, which may be removed by redistillation over a small quantity of trithioformaldehyde.

2. *From trithioformaldehyde and sulphur dichloride.* Sulphur

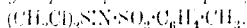
dichloride (73.3 grams, 2 mols.) is run on to powdered trithioformaldehyde (50 grams, 1 mol.), cooled in ice-water; hydrogen chloride is freely evolved and the mixture, after standing for fifteen minutes, is heated on the water-bath. On distillation under atmospheric pressure, much hydrogen chloride comes off and the temperature rises to 155° ; on fractional distillation through a Raschig dephlegmator, the product is resolved into pure carbon disulphide and $\alpha\alpha'$ -dichlorodimethyl sulphide. When the reaction mixture is directly distilled under reduced pressure, the carbon disulphide escapes condensation and $\alpha\alpha'$ -dichlorodimethyl sulphide, boiling at $55-56.5^{\circ}/17$ mm., is at once obtained, the yield being 97 per cent of that required by equation (2). The reaction thus proceeds practically quantitatively and the method of preparation now described is much to be preferred to that given by Bloch and Höhn.

$\alpha\alpha'$ -Dichlorodimethyl sulphide is a colourless liquid boiling at $57.5-58.5^{\circ}/18$ mm., and having the density d_4^{20} 1.4144; it does not solidify in an ice-salt mixture, but forms a hard, crystalline mass when cooled in a mixture of solid carbon dioxide and ether. It has no vesicant action on the skin. It reacts slowly with methyl iodide, giving a dark, viscous liquid from which no pure substance was isolated.

$\alpha\alpha'$ -Dichlorodimethyl Sulphoxide, $(\text{CH}_2\text{Cl})_2\text{SO}$.—On adding cold concentrated nitric acid to $\alpha\alpha'$ -dichlorodimethyl sulphide, vigorous oxidation soon sets in, but the product yields but little of the sulphoxide. The latter is readily prepared by adding the dichlorosulphide slowly to an agitated mixture of fuming (2 vols.) and concentrated (1 vol.) nitric acids, cooled in ice and salt; oxidation proceeds smoothly in the cold, after which the clear solution is diluted, neutralised, and extracted several times with chloroform. The chloroform extract yields a crystalline residue on evaporation; the pure sulphoxide is obtained by crystallisation from carbon tetrachloride in colourless plates melting at 40° (Found: C = 16.5; H = 2.8; Cl = 48.5. $\text{C}_2\text{H}_4\text{OCl}_2\text{S}$ requires: C = 16.3; H = 2.7; Cl = 48.2 per cent.).

No crystalline nitrate corresponding to that formed by dimethyl sulphoxide could be prepared.

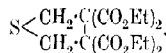
$\alpha\alpha'$ -Dichlorodimethylsulphine-*p-toluenesulphonylimine*,



—On shaking a concentrated aqueous solution of hydrated chloramine T (5 grams) with $\alpha\alpha'$ -dichlorodimethyl sulphide (2.4 grams) a solid substance soon separates; this after standing is separated, washed with water, dried, and crystallised from benzene; the pure sulphilimine is obtained in colourless needles melting at 102° on crystallisation from dry ether (Found: C = 36.1; H = 3.8;

Cl = 23.6. $C_9H_{11}O_2NCl_2S_2$ requires C = 36.0; H = 3.7; Cl = 23.6 per cent.).

Ethyl Tetrahydrothiophen-3:3:4:4-tetracarboxylate,



—Ethyl ethanetetracarboxylate (15.9 grams) is dissolved in a solution of sodium (2.3 grams) in absolute alcohol (250 c.c.), $\alpha\alpha'$ -dichlorodimethyl sulphide (6.55 grams) added, and the solution boiled under a reflux for three hours; after filtering from sodium chloride and evaporating the filtrate, the residual syrup is distilled under reduced pressure through a short column. The major fraction distils at $220-223^\circ/15$ mm. as a viscous syrup which does not crystallise in an ice-salt mixture and constitutes the pure *ethyl tetrahydrothiophen-3:3:4:4-tetracarboxylate* (Found: C = 50.7; H = 6.52; S = 8.68. $C_{16}H_{24}O_8S$ requires C = 51.0; H = 6.43; S = 8.52 per cent.). This ester is recovered unchanged after boiling for nine hours with 18 per cent. sulphuric acid or for seven hours with 7 per cent. aqueous alcoholic potash; it appears to be hydrolysed by prolonged boiling with 10 per cent. aqueous potash, but no tetrahydrothiophen derivative could be separated from the product.

$\alpha\alpha'$ -Dichlorodiethyl Sulphide, $S(CHCl \cdot CH_3)_2$.—1. From α -trithioacetaldehyde and sulphur monochloride.—On adding sulphur monochloride (55.7 c.c.) to powdered α -trithioacetaldehyde (96 grams), solution occurs and the liquid becomes warm; on heating on the water-bath for ninety minutes, a little hydrogen chloride is evolved. On distillation under diminished pressure, a colourless fraction (39 grams) distils up to $75^\circ/28$ mm.; this is nearly pure $\alpha\alpha'$ -dichlorodiethyl sulphide and represents a yield of about 45 per cent. of that required by an equation of the form of that numbered (1). When this fraction has been taken off, the residue begins to foam, and evolves hydrogen chloride and a volatile product which possesses a sickening stench and cannot be condensed. A second fraction (14 grams) comes over at $75-110^\circ/32$ mm.; this is yellow in colour and fumes in the air. A final fraction (22 grams) is obtained at $110-115^\circ/30$ mm.; this is red and also fumes in the air. A considerable tarry residue is left in the distilling flask.

The first fraction, when redistilled through a Raschig column, gives the pure $\alpha\alpha'$ -dichlorodiethyl sulphide as a colourless liquid boiling at $54-56^\circ/15$ mm. (Found: C = 30.3; H = 5.1; Cl = 44.8. Calc., C = 30.2; H = 5.1; Cl = 44.6 per cent.).

The yellow and red fractions, when redistilled through the column under diminished pressure, undergo considerable decomposition, leaving a tarry residue which is violently oxidised by cold nitric

acid; an individual product is obtained in quantity at 88—91°/14 mm. and represents the diethylidene trisulphide described below.

2. *From α -trithioacetaldehyde and sulphur dichloride.*—On adding sulphur dichloride (45.5 grams) to α -trithioacetaldehyde (40 grams), an almost colourless solution results and slowly evolves hydrogen chloride when heated on the water-bath. When it is distilled under diminished pressure, $\alpha\alpha'$ -dichlorodiethyl sulphide (10 grams) and diethylidene trisulphide (4 grams) are obtained as in the reaction with sulphur monochloride; again, however, a large, viscous residue is left in the flask and decomposes profoundly on further heating. It will be seen that the best yields of $\alpha\alpha'$ -dichlorodiethyl sulphide and of diethylidene trisulphide result from the use of sulphur monochloride.

$\alpha\alpha'$ -Dichlorodiethyl sulphide is a colourless liquid possessing an unpleasant musty odour and having no vesicant action on the skin; it boils at 56—57°/16 mm., at 66.5—67.5°/27 mm., and at 76—77°/41 mm., and has the density d_4^{20} 1.1992. These determinations are in good accord with the constants given by Bales and Nickelson (*loc. cit.*). It is interesting to note that the isomeric $\beta\beta'$ -dichlorodiethyl sulphide has an appreciably greater density and higher boiling point; Gibson and Pope (T., 1920, 117, 276) give the density d_4^{20} 1.285, and the boiling point has been determined as 107—108°/16 mm. The $\alpha\alpha'$ -isomeride does not solidify on immersion in an ice-salt mixture, but forms a hard, crystalline mass when cooled in a mixture of solid carbon dioxide and ether; it is less stable than the $\beta\beta'$ -isomeride and soon commences to evolve hydrogen chloride on exposure to the air, although it can be preserved indefinitely in a dry atmosphere. Attempts to prepare the corresponding sulfoxide were unsuccessful; the sulphide is oxidised vigorously by nitric acid, and a burst of flame results when it is dropped into fuming nitric acid. Numerous attempts to moderate the oxidation of the compound by nitric acid merely yielded solutions from which oxalic acid was separable as the most important product.

Unlike its lower homologue, $\alpha\alpha'$ -dichlorodiethyl sulphide could not be converted into a sulphilimine with chloramine T, only *p*-toluenesulphonamide being produced during the reaction; further, no condensation product of the sulphide with ethyl ethanetetracarboxylate could be obtained.

$\alpha\alpha'$ -Dithioethylidene Sulphide. (OEt·CHMe)₂S. $\alpha\alpha'$ -Dichlorodiethyl sulphide (19.5 grams) is added to a solution of sodium (5.6 grams) in alcohol (250 c.c.) and the solution boiled for three hours; after separating the sodium chloride and evaporating off the alcohol, the residue is distilled under diminished pressure through a short

column. $\alpha\alpha'$ -Diethoxydiethyl sulphide is thus obtained in almost theoretical yield as a colourless liquid boiling at $87-87.5^\circ/21$ mm. (Found: C = 53.9; H = 10.4; S = 18.2. $C_8H_{18}O_2S$ requires C = 53.9; H = 10.2; S = 18.0 per cent.). The compound has but a faint odour, is vigorously oxidised by gold concentrated nitric acid, and does not yield a sulphilimine with chloramine T.

Diethyldiene Trisulphide, $S<\begin{smallmatrix} CHMe \\ CHMe \end{smallmatrix}>S'S$.—This substance, which is formed during the action of the sulphur chlorides on α -trithioacetaldehyde, was obtained after repeated fractionation as a pale green liquid which does not fume in the air and boils at $89-90^\circ/14$ mm. (Found: C = 31.6; H = 5.3; S = 62.6. $C_4H_8S_3$ requires C = 31.5; H = 5.3; S = 63.2 per cent.). Cold concentrated nitric acid immediately oxidises the compound with liberation of sulphur, so that the grouping $S'S$ is probably present; it inflames when dropped into fuming nitric acid. When diethyldiene trisulphide (2.2 grams) and methyl iodide (2.0 grams, 1 mol.) are mixed and the product is preserved in the dark for a week, it becomes almost black and develops an evil odour, whilst a crust of long needles is formed. The latter material, when separated and purified by crystallisation from alcohol, melts at 126° , and is proved by analysis and mixed melting-point determinations to be β -trithioacetaldehyde.

During the separation of $\alpha\alpha'$ -dichlorodiethyl sulphide and diethyldiene trisulphide from the product of the action of sulphur monochloride upon α -trithioacetaldehyde, intermediate fractions containing the first two compounds named are obtained: when these are preserved for a fortnight, they become semi-solid owing to the crystallisation of β -trithioacetaldehyde. This compound was identified by analysis and mixed melting-point determinations, and is formed by the interaction of $\alpha\alpha'$ -dichlorodiethyl sulphide and diethyldiene trisulphide.

Action of the Sulphur Chlorides on Thialdine and β -Trithiobenzaldehyde.—Sulphur monochloride acts violently upon thialdine, converting it into a black mass: the reaction may be moderated by working in carbon tetrachloride solution and cooling in ice-water, when a reddish-black solid separates and hydrogen chloride is evolved. On distillation under diminished pressure, only carbon tetrachloride distils and a voluminous black residue is left. A similar result is obtained when the sulphur monochloride is replaced by the dichloride.

β -Trithiobenzaldehyde dissolves in sulphur monochloride and no hydrogen chloride is evolved on heating on the water-bath: distillation under diminished pressure gives merely a little sulphur

monochloride and a very small amount of a purple oil. On substituting sulphur dichloride for the monochloride and warming, a little hydrogen chloride is evolved; on distillation under 21 mm. pressure, a small proportion of an oil is obtained which was found to consist largely of benzal chloride.

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[Received, April 4th, 1923.]

CXXXIV.—The Isomeric Trithioacetaldehydes.

By FREDERICK GEORGE MANN and WILLIAM JACKSON POPE.

WE have attempted to prepare the hitherto unknown cyclic diethylidene disulphide, $S < \begin{smallmatrix} \text{CHMe} \\ \text{CHMe} \end{smallmatrix} > S$, by the action of silver sulphide on alcoholic solutions of $\alpha\alpha'$ -dichlorodiethyl sulphide; the reaction readily yields a white, crystalline substance melting at 81° and having the empirical composition of diethylidene disulphide. On attempting to prepare the methiodide of this substance by treatment with methyl iodide, we obtained a compound which had the same empirical composition and melted at 126° , and which we have identified with β -trithioacetaldehyde; molecular-weight determinations indicated that the compounds melting at 81° and 126° are isomeric.

Marckwald obtained a crystalline compound of the composition $(C_2H_4S)_3$, melting at 76° , by boiling thialdine thiocyanate with water (*Ber.*, 1886, **19**, 1826), and showed later that this product, which he named γ -trithioacetaldehyde, was converted into β -trithioacetaldehyde by treatment with ethyl iodide (*Ber.*, 1887, **20**, 2817); Poleck and Thümmel (*Ber.*, 1889, **22**, 2871) found that hydrogen sulphide converts vinyl mercuric oxychloride into a compound melting at 75 – 76° , which is apparently identical with γ -trithioacetaldehyde.

The constitution $MeHC < \begin{smallmatrix} S\text{-CHMe} \\ S\text{-CHMe} \end{smallmatrix} > S$ is ordinarily assigned to the trithioacetaldehydes and, as Baumann and Frömm have pointed out (*Ber.*, 1891, **24**, 1419, 1457), the existence of two stereoisomides may be anticipated: they regard the α - and β -trithioacetaldehydes as possessing respectively the *cis*- and *trans*-configurations. The classification adopted by these authors provides no place for Marckwald's γ -trithioacetaldehyde, and they state that this latter is actually only an impure preparation of α -trithioacetaldehyde, which melts at 101° . The chief reason advanced by Baumann and Frömm for this conclusion is that their preparations of Marck-

wald's γ -isomeride, which melted at $71-77^\circ$, yielded pure α -trithioacetaldehyde, melting at 101° , when crystallised from acetone.

The product melting at 81° , which we have obtained, is undoubtedly isomeric with β -trithioacetaldehyde, into which it is converted by treatment with methyl iodide; we presume it to be a pure preparation of Marekwald's γ -trithioacetaldehyde, and we conclude that Baumann and Frömm were mistaken in disputing the existence of the third or γ -isomeride. That our compound is pure is shown by the fact that we obtain it of the same melting point, 81° , by four methods, namely, by the action of silver oxide, sodium hydroxide, silver sulphide, and hydrogen sulphide on $\alpha\alpha'$ -dichlorodiethyl sulphide, and that it sublimes without change in melting point. It should be noted further that the melting point of our preparations of γ -trithioacetaldehyde is not affected by recrystallisation from acetone.

It has been shown (this vol., p. 1177) that diethylidene trisulphide is converted into β -trithioacetaldehyde when treated with methyl iodide. The loss of sulphur which attends this conversion is not entirely without precedent, for Ráy has shown (F., 1922, **121**, 1279) that triethylene tetrasulphide on treatment with ethyl iodide, mercuric chloride, or platonic chloride yields derivatives of triethylene trisulphide. Our diethylidene trisulphide is probably identical with an oil obtained by Klinger (*Ber.*, 1878, **11**, 1925) on treating monomolecular thioacetaldehyde with water and to which he assigned the composition $8C_2H_4S_3H_2S$; Klinger found that addition of a drop of acetaldehyde converted the oil into α -trithioacetaldehyde, whilst solution in sulphuric acid and precipitation by water yielded β -trithioacetaldehyde and sulphur. Suyver showed (*Rec. trav. chim.*, 1905, [ii], **24**, 377) that α -trithioacetaldehyde is partially converted into the β -isomeride by treatment with ethyl iodide and other reagents.

EXPERIMENTAL.

Preparation of γ -Trithioacetaldehyde.—1. *By the action of silver sulphide on $\alpha\alpha'$ -dichlorodiethyl sulphide.* A solution of $\alpha\alpha'$ -dichlorodiethyl sulphide (17.0 grams) in alcohol (20 c.c.) is slowly added to an excess of precipitated silver sulphide (31.0 grams) suspended in alcohol (75 c.c.) and maintained at 0° . After standing for fifteen minutes, the solution is boiled for five hours under a reflux and then filtered hot, the precipitate being washed with a little hot alcohol. Warm water (10 c.c.) is added to the filtrate, which on cooling deposits the trithioaldehyde as a white, crystalline powder; a further deposit is obtained by pouring the filtrate from this into

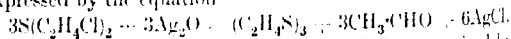
twice its volume of ice-water. The crude product (8.0 grams), assuming that three molecules of the chlorinated ethyl sulphide give two of the trithioacetaldehyde, represents a yield of about 60 per cent. of the theoretical.

The crude product is recrystallised from hot 85 per cent. alcohol and then, to remove traces of occluded silver compounds, from light petroleum (b. p. 40–60°); on spontaneous evaporation of the solvent, γ -trithioacetaldehyde is deposited in small, white crystals melting at 80°. A very small proportion of the β -isomeride crystallises at the same time in long needles melting at 124–125°.

2. *By the action of hydrogen sulphide on $\alpha\alpha'$ -dichlorodiethyl sulphide.* A purer product is more readily prepared by passing dry hydrogen sulphide through a solution of $\alpha\alpha'$ -dichlorodiethyl sulphide in twice its volume of alcohol: no change is apparent, but after standing over-night the solution becomes a semi-solid crystalline mass. On filtering and washing with a little alcohol, γ -trithioacetaldehyde is obtained in small, white crystals melting at 81° (Found: C = 46.5; H = 6.78; S = 53.6; M_r by cryoscopic method in benzene, = 171, 172. $C_6H_{12}S_3$ requires C = 40.0; H = 6.71; S = 53.3 per cent.; $M = 180$). A mixture of this preparation with that made by the silver sulphide method melted at 80.5°.

3. *By the action of silver oxide on $\alpha\alpha'$ -dichlorodiethyl sulphide.* Dry silver oxide reacts vigorously with a cold alcoholic solution of $\alpha\alpha'$ -dichlorodiethyl sulphide, heat being evolved and a smell of acetaldehyde becoming apparent, whilst γ -trithioacetaldehyde is produced. The reaction may be moderated by adding $\alpha\alpha'$ -dichlorodiethyl sulphide (6.7 grams), dissolved in alcohol (20 c.c.), to a suspension of silver oxide (9.7 grams) in alcohol (25 c.c.) maintained at 0° for half an hour. After boiling for four hours under a reflux and filtering, cooling, and diluting as above described, γ -trithioacetaldehyde (1.85 grams) is obtained and this, after recrystallisation, melts at 80°; this melting point is unchanged when the product is mixed with a little of the substance prepared by the silver sulphide method.

Since no evidence of the formation of the stable dimethyl-1:3-thioxan (Markwald, *loc. cit.*) boiling at 166–168° could be obtained, and since acetaldehyde was found in the first runnings obtained by distilling the alcoholic mother-liquors from the preparation, it seems that the action of silver oxide on $\alpha\alpha'$ -dichlorodiethyl sulphide is expressed by the equation



The yields obtained are about 70 per cent. of those required by this equation.

4. *By the action of sodium hydroxide on $\alpha\alpha'$ -dichlorodiethyl sulphide.* When $\alpha\alpha'$ -dichlorodiethyl sulphide is boiled for some time with sodium hydroxide (2 mols.) in aqueous solution and the liquid cooled, a heavy, semi-solid oil separates; this latter, when drained on a plate and crystallised from 85 per cent. alcohol, yields pure γ -trithioacetaldehyde melting at 81° . The action of sodium hydroxide is thus similar to that of silver oxide.

γ -Trithioacetaldehyde has a faint unpleasant odour—not an extremely strong one as described by Marckwald—which is much less noticeable than that of diethylene disulphide. It dissolves readily in all common organic solvents and crystallises best from 85 per cent. alcohol; it sublimes readily at 100° , yielding long needles melting at 81° . Its melting point is unchanged on crystallisation from, or by one hour's boiling with, acetone, so that Baumann and Frömm's statement that it gives the α -isomeride on such treatment is incorrect.

Conversion of γ - into β -Trithioacetaldehyde.— γ -Trithioacetaldehyde dissolves when heated at 30° with three molecular proportions of methyl iodide, and the solution, after several days' standing, deposits a mass of felted needles; these on recrystallisation from hot alcohol melt at 126° (Found: C = 40.2; H = 6.77; S = 53.0; M , by cryoscopic method in benzene, = 168, 171. Calc. for $C_6H_{12}S_3$, C = 40.0; H = 6.71; S = 53.3 per cent.; M = 180). This substance does not depress the melting point of β -trithioacetaldehyde prepared by the method of Baumann and Frömm (*Ber.*, 1889, 22, 2600); no doubt can therefore exist concerning the identity of the two products.

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[Received, April 4th, 1923.]

CXXXV.—*The Sulphides of Ammonium.*

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ALTHOUGH aqueous solutions containing ammonium hydrosulphide and ammonium monosulphide, and, indeed, polysulphides also, are largely employed in analytical operations, these substances are not well known in the anhydrous condition; some have never been isolated, and it is extremely doubtful if others, descriptions of which appear in the literature, have ever been obtained in the pure state.

Bineau (*Ann. Chim. Phys.*, 1838, [ii], 67, 225) obtained ammonium hydrosulphide in the form of colourless needles and plates by

mixing ammonia and hydrogen sulphide in approximately equal proportions by volume, and Bloxam (*Chem. News*, 1893, **68**, 97) showed that, provided there was no excess of ammonia, the ammonium hydrosulphide thus obtained was pure. Attempts to obtain the substance by the use of non-aqueous solvents do not appear to have been successful. Bloxam (T., 1895, **67**, 283) passed hydrogen sulphide into alcoholic solutions of ammonia, but the crystals he obtained invariably had the composition $(\text{NH}_4)_2\text{S}_n\text{NH}_4\text{HS}$, together with varying amounts of alcohol. Bineau's method, therefore, still remained the only satisfactory method of preparing ammonium hydrosulphide.

The monosulphide is still more obscure. Bineau (*Ann. Chim. Phys.*, 1839, [ii], **70**, 261) described its preparation by the interaction of two volumes of ammonia and one volume of hydrogen sulphide at -18° . Bloxam states, however (*loc. cit.*), that the mica-like crystals thus obtained have the composition $(\text{NH}_4)_2\text{S}_n\text{NH}_4\text{HS}$ and that in the presence of large excess of ammonia an oily liquid having the composition $(\text{NH}_4)_2\text{S}_2\text{NH}_3$ is formed. By carefully adjusting the volumes of the reacting gases and also their rates of flow, Bloxam claimed to have obtained micaceous crystals of ammonium monosulphide, but his description leaves no doubt that these crystals were always contaminated to a greater or less extent with ammonium hydrosulphide.

The present authors had as their primary object the preparation of polysulphides of ammonium by the method successfully employed by Rule and Thomas (T., 1911, **99**, 558; 1913, **103**, 871; 1914, **105**, 177) in their work on the polysulphides of sodium and potassium. This method of preparation is based on the action of the hydrosulphide in dry alcohol on sulphur, and, since ammonium hydrosulphide in alcoholic solution thus became the starting point in the preparation of the ammonium polysulphides, it seemed desirable at the same time to attempt the preparation of this substance, and also the monosulphide, in the anhydrous condition.

EXPERIMENTAL.

Ammonium Hydrosulphide.

The alcohol employed was dried by keeping it for twenty-four hours over freshly burned quicklime and then distilling it. The ammonia and the hydrogen sulphide were also carefully dried, the former by means of quicklime and the latter, after washing with water, by passing it through a long tube filled with calcium chloride.

A stock solution of ammonia in alcohol was prepared and a number of experiments were carried out in which dry hydrogen

sulphide was added, the relative amount of the gas, its rate of flow, and the temperature being varied. The crystals which separated from the solution took the form of large, glistening plates; they were rapidly collected, washed with dry ether, and analysed.

The ammonia was estimated by direct titration with standard acid, using methyl-orange as indicator. The sulphur also was estimated volumetrically. An excess of $N/10$ -iodine was added, the excess being then estimated by means of $N/10$ -sodium thio-sulphate. Preliminary experiments, in which the results obtained by this method were compared with those obtained when, after oxidising with bromine, the sulphur was precipitated and weighed as barium sulphate, proved this method to be sufficiently accurate.

Mention has already been made of Bloxam's attempt to prepare ammonium hydrosulphide by the action of hydrogen sulphide on alcoholic solutions of ammonia. He concluded that the crystals obtained were always complexes of the type $(\text{NH}_4)_2\text{S}_x\cdot n\text{NH}_4\text{HS}\cdot x\text{C}_2\text{H}_5\cdot\text{OH}$, and that the method was useless for the preparation of pure ammonium hydrosulphide. In the present investigation, the composition of the crystals obtained was found to vary considerably, but there seems to be little evidence of the formation of definite complexes. The solutions appear to contain both ammonium hydrosulphide and ammonium monosulphide in equilibrium with each other, and from them, by choosing the most suitable conditions, not only the pure hydrosulphide, but the monosulphide also, can be obtained.

In one experiment, 100 c.c. of an alcoholic solution of ammonia, containing 53 grams of ammonia per litre, were treated with dry hydrogen sulphide until the gas ceased to be absorbed. The solution became faintly yellow and a mass of large, glistening crystals was deposited. These were collected, washed, and analysed [Found: $\text{NH}_3 = 29.25$; $\text{H}_2\text{S} = 40.81$; molecular ratio 1.43. $(\text{NH}_4)_2\text{S}_x\cdot n\text{NH}_4\text{HS}\cdot x\text{C}_2\text{H}_5\cdot\text{OH}$ requires $\text{NH}_3 = 30.87$; $\text{H}_2\text{S} = 41.32$ per cent.; ratio 1.5].

These crystals undoubtedly contained ammonium hydrosulphide, for on dissolving them in water and adding sulphur to the solution hydrogen sulphide was evolved and a deep red solution obtained. The monosulphide does not behave in this manner.

The reaction between ammonia and hydrogen sulphide is exothermic and the solution rapidly becomes warm, much hydrosulphide being lost by volatilisation. On passing the escaping gases through a cooled vessel, beautiful crystals of ammonium hydrosulphide were deposited therein, the quantity depending on the rate of flow of the hydrogen sulphide and on the temperature.

In the next series of experiments, the solution was kept at 0° and the hydrogen sulphide passed in slowly. Dense masses of crystals were deposited, which were collected rapidly, washed with a little cold alcohol, and dried by suction. During the drying process much of the solid dissociated and was lost (Found : $\text{NH}_3 = 35.34$; $\text{H}_2\text{S} = 58.80$ per cent.). The substance probably still contained alcohol, but the molecular ratio of ammonia to hydrogen sulphide is that theoretically required for $(\text{NH}_4)_2\text{S} \cdot 4\text{NH}_4\text{HS}$, namely, 1:20. Notwithstanding this agreement, the authors do not feel justified in looking on this substance as a definite compound. On performing the experiment again under similar conditions, slightly different ratios were always obtained. The ratio was, however, always smaller when the crystals were prepared at low temperatures, although in no case was the value 1, corresponding to pure hydrosulphide, obtained. Moreover, it was found impossible completely to free the crystals from alcohol. Attempts were made to obtain them in the pure state by keeping them over various absorbents in an atmosphere of hydrogen sulphide, but without success.

When the crystals obtained in the experiment just described were repeatedly washed with small quantities of alcohol, a substance was obtained in which the ratio $[\text{NH}_3] : [\text{H}_2\text{S}]$ was approximately 1. A large quantity of the crystals was therefore sealed up with 20 c.c. of alcohol and kept at 25°. After twenty-four hours, the solution was filtered and the ratio $[\text{NH}_3] : [\text{H}_2\text{S}]$ was determined in both crystals and liquid. This process was repeated several times and the results obtained are given in the following table.

TABLE I.

Substance.	$[\text{NH}_3] : [\text{H}_2\text{S}]$	Substance.	$\text{NH}_3 : \text{H}_2\text{S}$
Original crystals	1:20	(Crystals after second wash	1:673)
(Crystals after first wash	1:12)	(Wash alcohol	1:235)
(Wash alcohol	1:38)	(Crystals after third wash	0:931)
		(Wash alcohol	1:027)

The crystals finally obtained were dried as far as possible from alcohol and analysed (Found : $\text{NH}_3 = 31.52$; $\text{H}_2\text{S} = 65.92$; ratio 0.96. NH_4HS requires $\text{NH}_3 = 33.33$; $\text{H}_2\text{S} = 66.66$ per cent.; ratio 1).

Thus the crystals would appear to be ammonium hydrosulphide; they still contain about 3 per cent. of alcohol, however, and this could not be removed.

Unlike the hydrosulphides of sodium and potassium, ammonium hydrosulphide, when precipitated from solution in alcohol by the addition of ether, was also found to contain alcohol, which could

not be removed by washing with ether. The method employed by Rule (T., 1911, 99, 558) for the preparation of the anhydrous hydrosulphides of the alkali metals is, therefore, not applicable to the preparation of ammonium hydrosulphide.

In the opinion of the present authors, anhydrous ammonium hydrosulphide is best obtained by alternately passing dry ammonia and dry hydrogen sulphide into carefully dried ether. In an experiment, beautiful white crystals were obtained which were collected by the aid of the pump and rapidly dried. After standing over paraffin wax in a desiccator for some days, they were analysed. The crystals dissociate very rapidly at room temperature and therefore low results were to be expected (Found : $\text{NH}_3 = 33.23$; $\text{H}_2\text{S} = 66.08$ per cent.; ratio 1.006).

As obtained in this way, ammonium hydrosulphide is a pure white substance consisting of a mass of fine, needle-shaped crystals. It dissociates rapidly and can only be kept in sealed vessels. It is insoluble in ether or benzene, but readily dissolves both in water and in alcohol, forming colourless solutions which rapidly turn yellow owing to oxidation and the consequent formation of polysulphides. After some time, sulphur is deposited from these solutions and on examination they were found to contain thiosulphate also. When an alcoholic solution of ammonium hydrosulphide is heated, it turns brown and sulphur is deposited in monoclinic crystals. It is interesting to notice that, according to Wetherill (*Amer. J. Sci.*, 1865, [ii], 40, 338), if a small amount of rhombic sulphur is initially present the sulphur deposited will be in the rhombic form.

When solutions of ammonium hydrosulphide in alcohol are treated with sulphur, hydrogen sulphide is evolved and the sulphur is dissolved, ammonium pentasulphide being formed. In this respect, therefore, ammonium hydrosulphide resembles potassium hydrosulphide.

Ammonium Monosulphide.

This substance is stated by Bloxam (*loc. cit.*) to be deposited in the form of micaceous crystals when hydrogen sulphide is mixed with considerable excess of ammonia at -18° . It is clear, however, from his description that the product obtained by Bloxam was always contaminated to a considerable extent with hydrosulphide, and the present authors have been unable to obtain ammonium monosulphide free from hydrosulphide by this method.

In the course of experiments in which attempts were made to prepare the hydrosulphide by the action of hydrogen sulphide on solutions of ammonia in alcohol, it was observed that the ratio $[\text{NH}_3]/[\text{H}_2\text{S}]$ in the liquid was very much higher when the temper-

ature was allowed to rise than when the solution was cooled during the passage of the gas. On the addition of ether to these solutions, a precipitate was obtained the composition of which varied with the composition of the solution, and it thus appeared that ammonium monosulphide might be obtained from such solutions by fractional precipitation with ether.

In an experiment, 300 c.c. of the stock ammonia solution were treated with a rapid stream of hydrogen sulphide. The temperature rose to 58° , and no crystals were deposited. The ratio $[\text{NH}_3]/[\text{H}_2\text{S}]$, determined in the solution by titration, was found to be 1.84. That this solution contained but little hydrosulphide was shown by the fact that it would not dissolve sulphur at all readily, the solution thus obtained being only pale yellow in colour.

On adding ether to the solution just described, a heavy, white precipitate was immediately thrown down. Three specimens were obtained by the successive addition of three amounts of ether, each of 100 c.c. On determining the ratio $[\text{NH}_3]/[\text{H}_2\text{S}]$ in these precipitates, the following values were found (a) 1.15, (b) 1.097, (c) 1.051. It is obvious, therefore, that hydrosulphide only is obtained by this method of procedure. This result can be explained by the great readiness with which ammonium monosulphide dissociates into the hydrosulphide and free ammonia.

Since ammonia is very readily soluble in ether, it is in the highest degree probable that, even although the monosulphide were first formed, the addition of a considerable quantity of ether would favour its dissociation, and this view was supported by the observation that the ratio $[\text{NH}_3]/[\text{H}_2\text{S}]$ was somewhat higher when smaller quantities of ether were employed.

A similar experiment was therefore made, in which, instead of pure ether, ether saturated with ammonia was used as the precipitating agent. The ratio in the original alcoholic solution was 1.93, and, as before, three precipitates were obtained by the addition of three successive amounts of 100 c.c. each of the precipitating liquid. These precipitates were analysed, a matter of great difficulty, owing to the rapidity with which dissociation took place. In the first instance, the ratio was determined by dissolving a quantity of the material in water and estimating the ammonia and the hydrogen sulphide in the solution by the methods already described. The ratios for the three precipitates were thus found to be 1.77, 1.86, and 1.91, respectively. These crystals were different in appearance from the ammonium hydrosulphide obtained in the previous experiment. They seemed to be transparent cubes and they decomposed very much more readily, giving off ammonia copiously, but apparently very little hydrogen sulphide. An

attempt was made to obtain the exact composition of the crystals by transferring them rapidly to a weighing bottle, weighing, and then opening the weighing bottle under water [Found : $\text{NH}_3 = 28.21$; $\text{H}_2\text{S} = 29.81$; ratio 1.893. $(\text{NH}_4)_2\text{S} \cdot \text{C}_2\text{H}_5 \cdot \text{OH}$ requires $\text{NH}_3 = 29.83$; $\text{H}_2\text{S} = 29.83$ per cent.; ratio 2]. In view of the fact that ammonia was certainly lost during the weighing of the substance, the authors feel justified in regarding it as ammonium monosulphide combined with one molecule of alcohol of crystallisation.

In another experiment, a large quantity of ether, saturated with ammonia, was added to an alcoholic solution in which the ratio $[\text{NH}_3]/[\text{H}_2\text{S}]$ was 1.93 and which had been cooled in a freezing mixture. The result was interesting. In this case, no crystals were obtained, but a heavy, highly refracting oil of a light yellow colour separated out. Bloxam obtained a similar oil by mixing hydrogen sulphide with an excess of ammonia at -18° . On analysis, the liquid was found still to contain alcohol, but the value 3.7 was obtained for the ratio $[\text{NH}_3]/[\text{H}_2\text{S}]$, and this is in fair agreement with the formula $(\text{NH}_4)_2\text{S} \cdot 2\text{NH}_3$ assigned by Bloxam to the substance obtained by him. This compound was subsequently obtained in a state of purity by a method presently to be described.

The action of hydrogen sulphide on solutions of ammonia in ether has already been shown to yield ammonium hydrosulphide. Attempts were next made to convert this substance into the monosulphide by shaking it with ether which was kept constantly saturated with ammonia. In one experiment, 200 c.c. of ether were saturated with ammonia, the containing vessel being immersed in ice. Hydrogen sulphide was then passed into the cooled liquid until no more appeared to be absorbed. A further 200 c.c. of ether was then added and the liquid again saturated with ammonia. A small quantity of the precipitate was then removed in which the ratio $[\text{NH}_3]/[\text{H}_2\text{S}]$ was determined, and the vessel was then set aside in a cool place and was shaken at intervals. From time to time, specimens of the precipitate were removed and analysed, more ammonia being at the same time passed into the liquid, which was thus kept saturated with the gas. The results given below indicate that some monosulphide was formed, for the ratio $[\text{NH}_3]/[\text{H}_2\text{S}]$ was found to increase. The rate of increase was, however, extremely slow, probably because of the exceedingly slight solubility of ammonium hydrosulphide in ether. After five days, the ratio had reached the value 1.39, but the increase in the last two days only amounted to 0.03, and no further determinations were made.

TABLE II.

Time in days.	$[\text{NH}_3]/[\text{H}_2\text{S}]$.	Increase in ratio.
0	1.035	—
1	1.23	0.195
2	1.32	0.09
3	1.36	0.04
5	1.39	0.03

At this point, 2 c.c. of alcohol were added and the vessel was immersed in a freezing mixture, the temperature of the liquid falling to -10° . The liquid was left over-night, and in the morning a considerable quantity of yellow oil had separated, suspended in which were a few fairly large, transparent crystals, apparently cubical in form. The oil was analysed in the following way. Through the cork closing the neck of the conical flask in which the preparation had been made a tube was introduced, the end of which projected into the oil, but remained above the crystals. Outside the flask, the tube was provided with two stopcocks, between which a small bulb had been blown. Before the experiment, the tube was weighed. On opening the taps, the pressure in the apparatus forced oil into the bulb and as soon as sufficient had been collected the taps were again closed. During this stage, it was found advantageous to surround that portion of the tube which was outside the flask with a freezing mixture. When everything was ready, the tube was withdrawn and carefully cleaned. It was then weighed, opened under water, and the ammonia and the hydrogen sulphide estimated in the manner previously described [Found: $\text{NH}_3 = 66.16$; $\text{H}_2\text{S} = 33.27$; ratio 3.97. $(\text{NH}_4)_2\text{S} \cdot 2\text{NH}_3$ requires $\text{NH}_3 = 66.66$; $\text{H}_2\text{S} = 33.33$ per cent.; ratio 4].

When kept in an open vessel, the oil rapidly decomposed and transparent, cubic crystals were deposited which in turn very quickly dissociated. These crystals appeared to be identical in composition with those observed accompanying the oil immediately after its preparation.

Several attempts were made to obtain an accurate analysis of these crystals, but the rapidity with which they decompose and the difficulty of obtaining them quite free from liquid rendered this impossible. Several determinations of the ratio $[\text{NH}_3]/[\text{H}_2\text{S}]$ were made, however, yielding values varying between 1.92 and 2.11. Here, again, accurate results could not be expected. From the method of preparation, however, these crystals could not contain alcohol and the authors believe them to consist of anhydrous ammonium monosulphide.

Summary.

1. The solutions obtained by the action of hydrogen sulphide on alcoholic solutions of ammonia contain both ammonium hydrosulphide and monosulphide in equilibrium with each other and from them crystals of varying composition separate. No evidence was obtained of the formation of solid complexes.

2. Low temperatures favour the formation of the hydrosulphide in the solution, the monosulphide being mainly produced when the temperature is allowed to rise. Nearly pure hydrosulphide was obtained by crystallising a solution prepared at 0° and rapidly washing the crystals with small quantities of dry alcohol. On fractionally precipitating solutions, the temperature of which had been allowed to rise, with ether saturated with ammonia, crystals of the monosulphide with one molecule of alcohol of crystallisation were obtained.

3. Anhydrous ammonium hydrosulphide is best prepared by alternately passing ammonia and hydrogen sulphide into dry ether.

4. Attempts to convert the hydrosulphide into the monosulphide by the prolonged action of saturated solutions of ammonia in ether failed, but in the presence of a small quantity of alcohol a yellow oil having the composition $(\text{NH}_4)_2\text{S} \cdot 2\text{NH}_3$ separated out, together with a few transparent, cubic crystals, believed to be anhydrous ammonium sulphide. Similar crystals were obtained when the oil was kept in an open vessel. The ratio $[\text{NH}_3] : [\text{H}_2\text{S}]$ was determined for these crystals, the results lying between 1.92 and 2.11. In view of the great difficulty of obtaining an accurate analysis, this is considered to be in good agreement with the value 2 required by theory for $(\text{NH}_4)_2\text{S}$.

In conclusion, the authors desire to express their thanks to Professor E. C. C. Baly, C.B.E., F.R.S., for granting facilities for carrying out the work and for much kindly help and criticism during its progress; and also to Mr. J. H. Jones, B.Sc., and Mr. H. Evers, B.Sc., who made some of the preparations.

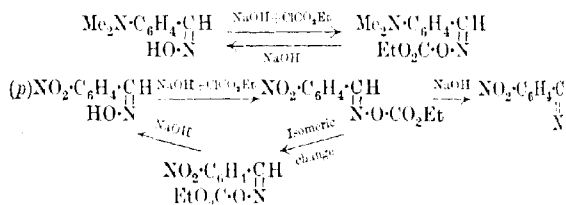
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[Received, March 27th, 1925.]

XXXXVI.—*The Isomerism of the Oximes. Part XI, Carbethoxy-derivatives.*

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THE study of the carbethoxy-derivatives of the oximes was commenced by Dunn and one of us some eight years ago. Circumstances, however, prevented its completion, and the action of ethyl chloroformate on the sodium salts of but three oximes was studied. It was found (T., 1916, **109**, 678) that *m*-nitro- and *p*-dimethylamino-benzantialdoximes in sodium hydroxide solution on shaking with ethyl chloroformate gave carbethoxy-derivatives which, on hydrolysis with hot sodium hydroxide solution, regenerated the original oximes, but that *p*-nitrobenzantialdoxime, on similar treatment, gave a carbethoxy-compound (m. p. 94°) which on hydrolysis gave *p*-nitrobenzonitrile. When this derivative was boiled with alcohol, isomeric change took place and another carbethoxy-compound was obtained (m. p. 109°) which on hydrolysis gave *p*-nitrobenzantialdoxime. On the basis of the Hantzsch-Werner stereochemical hypothesis for the isomerism of the oximes, it seemed reasonable to suppose that the derivatives which on hydrolysis regenerated the *anti*-oxime possessed the *anti*-configuration, and those which gave the nitrile in these circumstances the *syn*-configuration; indeed, this assumption, applied to the acetyl compounds, is the basis of Hantzsch's method for the determination of the configuration of aldoximes (Hantzsch and Miolati, *Z. physikal. Chem.*, 1892, **10**, 1; 1894, **13**, 509). The reactions were therefore represented as follows:



The possibility that, on the analogy of certain reactions of the ethylene derivatives, *trans*-elimination may take place more readily than *cis*-elimination has not been overlooked. If this were the case, all our formulæ for the oximes would have to be inverted, but until some direct evidence of *trans*-elimination among these compounds is forthcoming there seems to be no reason to introduce confusion by any departure from Hantzsch's original conception.

The action of ethyl chloroformate on an alkaline solution of *p*-nitrobenzantialdoxime resulted in a change of configuration, but this did not occur in the other two cases; although this inversion was not entirely novel (compare Brady and Dunn, T., 1913, **103**, 1613; 1916, **109**, 651), it seemed of sufficient importance in connexion with the mechanism of oxime change to justify further study of the action of ethyl chloroformate on aromatic aldoximes of various types. Of those which are known to exist in two isomeric forms, *o*-, *m*-, and *p*-chloro-, *o*-, *m*-, and *p*-nitro-, *p*-methoxy-, and 3:4-methylenedioxy-benzaldoximes and benzaldoxime itself have now been employed, whilst of those which, so far, have only been obtained in one form, besides *p*-dimethylaminobenzantialdoxime already investigated, *o*-methoxy-, 3-nitro-*p*-dimethylamino-, and 6-nitro-3:4-methylenedioxy-benzantialdoximes have been used. Although long experience has shown that oximes seldom behave as expected, the results obtained have been surprising, and are very difficult to interpret.

When acted upon in solution in 2*N*-sodium hydroxide with ethyl chloroformate, benzantialdoxime, *o*-, *m*-, and *p*-chloro-, *m*-nitro-, *p*-dimethylamino-, 3-nitro-*p*-dimethylamino-, 6-nitro-3:4-methylenedioxy-, and *o*-methoxy-benzantialdoximes all yield carbethoxy-derivatives which on hydrolysis regenerate the original oximes, and may therefore be assumed to have the *anti*-configuration. On the other hand, *p*-nitro-, *p*-methoxy-, and 3:4-methylenedioxy-benzantialdoximes under similar conditions give carbethoxy-compounds which on hydrolysis yield the corresponding nitriles, and may be supposed to be *syn*-derivatives. *o*-Nitrobenzantialdoxime, when acted upon in alkaline solution with ethyl chloroformate, gave *o*-nitrobenzonitrile direct, it being impossible to isolate an intermediate carbethoxy-compound. The carbethoxy-compound was, however, formed by the action of ethyl chloroformate on the dry silver salt of *o*-nitrobenzantialdoxime, and since dilute alkalis converted it into the nitrile it was apparently a *syn*-derivative. Whereas carbethoxy-*p*-nitrobenzsynaldoxime on boiling with alcohol was converted into carbethoxy-*p*-nitrobenzantialdoxime, the corresponding *o*-nitro-, *p*-methoxy-, and 3:4-methylenedioxy-compounds were not affected by such treatment. Attempts to prepare the carbethoxy-*anti*-derivatives of these oximes were unsuccessful, as the *syn*-derivatives were always obtained even by the action of ethyl chloroformate on the dry silver salts of the *anti*-oximes. There seems to be no reason for the differential action of ethyl chloroformate. Although three of the oximes which gave *syn*-derivatives were para-substituted, *o*-nitrobenzantialdoxime behaved in a similar way, except that its carbethoxy-derivative

was so unstable that the excess of alkali present caused immediate decomposition to *o*-nitrobenzonitrile. Moreover, *p*-dimethyl-amino-, 3-nitro-*p*-dimethylamino-, *p*-chloro-, and 6-nitro-3:4-methylenedioxy-benzantialdoximes suffered no change in configuration on conversion into their carbethoxy-derivatives.

When the substituted benzsynaldoximes were treated in alkaline solution with ethyl chloroformate, the invariable product of the reaction was the corresponding nitrile, no carbethoxy-compound being formed even in the cases of *p*-methoxy- and 3:4-methylenedioxy-benzsynaldoximes. This, apparently due to the hydrolysis of the carbethoxy-*syn*-derivative as formed, is somewhat remarkable, as carbethoxy-*p*-methoxy- and carbethoxy-3:4-methylenedioxy-benzsynaldoximes, when prepared from the *anti*-oximes, are precipitated in the presence of a similar excess of sodium hydroxide to that employed in the reaction with the *syn*-oximes. The phenomenon, however, is to a certain extent one of degree; carbethoxy-*o*-nitrobenzsynaldoxime is so sensitive to alkali that it is decomposed in the preparation from the *anti*-oxime; carbethoxy-*p*-methoxy- and carbethoxy-3:4-methylenedioxy-benzsynaldoximes are not so sensitive and are isolable when prepared from the *anti*-oximes, and can, moreover, be prepared from the *syn*-oximes by dissolving these in 2*N*-sodium hydroxide and shaking with a solution of ethyl chloroformate in ether so as to remove the compounds formed as much as possible from the influence of the alkali by solution in the ether layer. *p*-Nitrobenzsynaldoxime, however, still gave the nitrile by this method.

Finally, it may be mentioned that the same carbethoxy-derivative was obtained from the silver salt of 3:4-methylenedioxybenzsynaldoxime as from the *anti*-oxime in alkaline solution and that carbethoxy-*m*-nitrobenzsynaldoxime was obtained from the silver salt of *m*-nitrobenzsynaldoxime, although in this case the *anti*-oxime yielded carbethoxy-*m*-nitrobenzantialdoxime. There seemed, therefore, no reason to suppose that the abnormal behaviour was due to an inherent instability of some of the carbethoxy-compounds rather than to those compounds possessing in some cases the *anti*- and in others the *syn*-configuration, although in every case they were obtained from the *anti*-oximes.

The phenomena requiring explanation are, first, the formation in some cases of only *syn*-derivatives from *anti*-oximes, and, secondly, the formation of carbethoxy-*syn*-derivatives from *p*-methoxy-, 3:4-methylenedioxy-, and *p*-nitro-benzantialdoximes in the presence of excess of alkali, although under the same conditions the corresponding *syn*-oximes yield nitriles. The behaviour of the various oximes, however, seems so capricious both towards ethyl

chloroformate and other reagents of a similar type that it appears undesirable at the moment to attempt to answer the riddle.

EXPERIMENTAL.

Carbethoxybenzantialdoxime, $\begin{array}{c} \text{C}_6\text{H}_5\cdot\text{CH} \\ | \\ \text{EtO}_2\text{C}\cdot\text{O}\cdot\text{N} \end{array}$.—Five grams of benzantialdoxime were dissolved in 30 c.c. of 2*N*-sodium hydroxide and 4.5 grams of ethyl chloroformate slowly added with constant shaking and cooling. The oil which separated was extracted with ether, the solution dried over anhydrous sodium sulphate, and the ether removed at room temperature. The semi-solid mass so obtained had an odour of ethyl chloroformate and was pressed on a porous tile and washed thereon with a small quantity of ether. The solid carbethoxy-compound so obtained was crystallised with difficulty by dissolving in a small quantity of cold acetone and adding water drop by drop until a faint cloudiness appeared, scratching vigorously until crystallisation started, and then adding a few more drops of water cautiously to increase the amount of substance thrown out of solution. This method is called in subsequent descriptions crystallisation from acetone and water. With many oximes and their derivatives this proves to be an excellent method of purification, and possesses the advantage that it is unnecessary to heat the solution with the consequent risk of isomeric change. *Carbethoxybenzantialdoxime* crystallises in white needles melting at 34–35° (Found: N = 7.4. $\text{C}_{10}\text{H}_{11}\text{O}_3\text{N}$ requires N = 7.3 per cent.). The carbethoxy-compound was hydrolysed by heating on the water-bath with 2*N*-sodium hydroxide until it dissolved. The alkaline solution was saturated with carbon dioxide, when the characteristic odour of benzantialdoxime was observed, but, owing to the low melting point of this compound making it difficult to identify as such, it was not isolated. The solution was extracted with ether, the extract dried and saturated with hydrogen chloride, and the characteristic hydrochloride thereby precipitated was found to give benzgualdoxime on treatment with sodium carbonate solution.

Carbethoxy-o-chlorobenzantialdoxime, $\begin{array}{c} \text{C}_6\text{H}_4\text{Cl}\cdot\text{CH} \\ | \\ \text{EtO}_2\text{C}\cdot\text{O}\cdot\text{N} \end{array}$.—Five grams of *o*-chlorobenzantialdoxime were dissolved in 25 c.c. of 2*N*-sodium hydroxide and 3.5 grams of ethyl chloroformate added with constant shaking and cooling. The product was treated as in the case of carbethoxybenzantialdoxime and crystallised from light petroleum in long, silky, white needles melting at 47° (Found: N = 6.2. $\text{C}_{10}\text{H}_9\text{O}_3\text{NCl}$ requires N = 6.2 per cent.).

Carbethoxy-m-chlorobenzantialdoxime.—This was prepared from

m-chlorobenzantialdoxime in an analogous manner to the above and crystallised from acetone and water in large, white crystals melting at 37° (Found: N = 6.5. $C_{10}H_9O_3NCl$ requires N = 6.2 per cent.).

Carbethoxy-p-chlorobenzantialdoxime.—This compound, prepared in an analogous manner to the above from *p*-chlorobenzantialdoxime, crystallised from acetone and water in white prisms melting at 83° (Found: N = 6.3. $C_{10}H_9O_3NCl$ requires N = 6.2 per cent.).

Attempt to Prepare Carbethoxy-p-chlorobenzsynaldoxime.—Attempts were made to prepare this compound by the action of ethyl chloroformate on the silver salt of *p*-chlorobenzsynaldoxime (see carbethoxy-*m*-nitrobenzsynaldoxime below). These efforts were, however, frustrated by the ease with which the sodium salt of the *syn*-oxime hydrolysed in aqueous solution, which made it impossible to prepare the silver salt in the usual way.

Hydrolysis of the Carbethoxychlorobenzantialdoximes.—The three carbethoxy-compounds above were hydrolysed as in the case of the benzantialdoxime derivative. On saturating the alkaline solutions with carbon dioxide, the respective oximes were precipitated in each case and identified by the melting points and mixed melting points with the original oximes.

Carbethoxy-o-methoxybenzantialdoxime, $\begin{matrix} \text{MeO}\cdot\text{C}_6\text{H}_4\cdot\text{CH} \\ \text{EtO}_2\text{C}\cdot\text{O}\cdot\text{N} \end{matrix}$.—Five

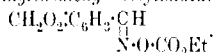
grams of *o*-methoxybenzantialdoxime, dissolved in 25 c.c. of 2*N*-sodium hydroxide, were treated as before with 4 grams of ethyl chloroformate. The derivative, isolated in the same way, crystallised from light petroleum in stout, colourless prisms melting at 52° (Found: N = 6.3. $C_{11}H_{13}O_4N$ requires N = 6.3 per cent.). Hydrolysis of this compound with 2*N*-sodium hydroxide, followed by precipitation with carbon dioxide, regenerated the original oxime.

Carbethoxy-p-methoxybenzsynaldoxime, $\begin{matrix} \text{MeO}\cdot\text{C}_6\text{H}_4\cdot\text{CH} \\ \text{N}\cdot\text{O}\cdot\text{CO}_2\text{Et} \end{matrix}$.—

Five grams of *p*-methoxybenzantialdoxime (anisaldoxime) were dissolved in 25 c.c. of 2*N*-sodium hydroxide and treated with 4 grams of ethyl chloroformate in the usual way. In this case, the carbethoxy-compound was deposited as a solid, which was separated by filtration instead of extraction with ether. It crystallised from acetone and water containing a small quantity of alcohol in white, glistening leaflets melting at 74° (Found: N = 6.5. $C_{11}H_{13}O_4N$ requires N = 6.3 per cent.). This compound was hydrolysed by heating on the water-bath with 2*N*-sodium hydroxide for an hour. Ammonia was evolved and on saturating the solution with carbon dioxide no oxime was precipitated. Acidification with dilute

hydrochloric acid resulted in the precipitation of anisic acid, identified by its melting point and mixed melting point with another specimen of that acid. Hydrolysis has consequently resulted in the production of anisonitrile and its further hydrolysis to the acid and ammonia. Carbethoxy-*p*-methoxybenzsynaldoxime was boiled for an hour under reflux with alcohol, but the original compound was recovered unchanged when the solution was diluted somewhat (compare carbethoxy-*p*-nitrobenzsynaldoxime, Brady and Dunn, *loc. cit.*). The same carbethoxy-*p*-methoxybenzsynaldoxime was obtained by shaking a solution of 5 grams of *p*-methoxybenzsynaldoxime in 25 c.c. of 2*N*-sodium hydroxide with 4 grams of ethyl chloroformate, dissolved in 25 c.c. of ether, for some time, separating the ether layer, and evaporating. In this way, the chance of hydrolysis of the carbethoxy-compound is minimised, as it is removed from the action of the alkali by solution in the ether.

Carbethoxy-3 : 4-methylenedioxybenzsynaldoxime.



—Three grams of 3 : 4-methylenedioxybenzsynaldoxime (piperonaldoxime) were dissolved in 40 c.c. of 2*N*-sodium hydroxide and treated with 2 grams of ethyl chloroformate as before. The solid which was precipitated was crystallised from acetone and water, when the carbethoxy-compound was obtained in large, white, irregular crystals melting at 78° (Found : N = 5.8. $\text{C}_{11}\text{H}_{11}\text{O}_5\text{N}$ requires N = 5.9 per cent.). Hydrolysed in the same manner as the carbethoxy-*p*-methoxybenzsynaldoxime, it gave no oxime, but 3 : 4-methylenedioxybenzoic acid, which was identified in the usual way. Boiling with alcohol under reflux for an hour did not bring about isomeric change, the original compound being recovered unaltered. A quantity of the solid carbethoxy-compound was melted on the water-bath for five hours : on cooling and crystallising the product from dilute alcohol, 3 : 4-methylenedioxybenzonitrile was obtained, being identified by the method of mixed melting points. Five grams of 3 : 4-methylenedioxybenzsynaldoxime were dissolved in dry ether, and 0.7 gram of sodium, dissolved in the minimum amount of alcohol, was added. The precipitated sodium salt was collected, washed with ether, dried, dissolved in water, and the calculated quantity (1 mol.) of silver nitrate added. The precipitated silver salt was collected, washed with water, pressed on a porous tile, and dried over sodium hydroxide in an evacuated desiccator. The silver salt so obtained was finely ground, suspended in dry ether, and three-fourths of the calculated quantity of ethyl chloroformate added. After leaving for forty-eight hours in the dark, the unchanged compound and silver chloride were removed

and the ethereal solution was evaporated at room temperature. A crystalline mass remained which after washing with a small quantity of ether was crystallised from acetone and water. The product so obtained was identical in properties with the carbethoxy-3:4-methylenedioxybenzsynaldoxime prepared by the first method, melting at 77° and not depressing the melting point of a specimen of that compound. Treatment of 3:4-methylenedioxybenzsynaldoxime in sodium hydroxide solution with a solution of ethyl chloroformate in ether in the manner described above for *p*-methoxybenzsynaldoxime also gave the same carbethoxy-compound, as did the treatment of the silver salt of the *syn*-oxime in an analogous manner to that of the *anti*-oxime.

Carbethoxy-*o*-nitrobenzsynaldoxime, $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\overset{\text{CH}}{\underset{\text{N}\cdot\text{O}\cdot\text{CO}_2\text{Et}}{\text{—}}}$ —When

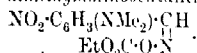
o-nitrobenzantaldoxime was treated in alkaline solution in the usual way with ethyl chloroformate, on one occasion a small quantity of a compound melting at 42° was obtained. All attempts to repeat this experiment were unsuccessful, as in every case the product which separated was found to be *o*-nitrobenzonitrile. The carbethoxy-derivative was, however, prepared by treating the dry silver salt of *o*-nitrobenzantaldoxime, obtained in the same manner as 3:4-methylenedioxybenzantaldoxime, in ethereal suspension with somewhat less than the calculated quantity of ethyl chloroformate for forty-eight hours. On filtering and evaporating the ethereal solution, a product was obtained which after pressing on a porous tile crystallised from alcohol and water in short, white, prismatic needles melting at 42° (Found: N = 11.9. $\text{C}_{10}\text{H}_9\text{O}_5\text{N}_2$ requires N = 11.8 per cent.). As is usually the case with acyl derivatives of *o*-nitrobenzantaldoxime, heating with 2*N*-sodium hydroxide resulted in profound decomposition of the carbethoxy-compound, but if a suspension in 2*N*-sodium hydroxide were left for two or three days at room temperature most of the compound passed into solution. After separating, the solid residue was crystallised from alcohol and found to consist of *o*-nitrobenzonitrile. The alkaline solution gave no precipitate of oxime when saturated with carbon dioxide, but when acidified with hydrochloric acid a precipitate of *o*-nitrobenzoic acid was obtained, which was identified in the usual way. When boiled under reflux with alcohol for an hour, carbethoxy-*o*-nitrobenzsynaldoxime was not converted into an *anti*-isomeride, the original compound being recovered. As in the case of *p*-chlorobenzsynaldoxime, the sodium salt of *o*-nitrobenzsynaldoxime was so readily hydrolysed by water that a satisfactory silver salt could not be obtained, and for this reason the action of ethyl chloroformate on this salt could not be studied.

Carbethoxy-m-nitrobenzsynaldoxime, $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\overset{\text{CH}}{\underset{\text{N}\cdot\text{O}\cdot\text{CO}_2\text{Et}}{\parallel}}\text{—The}$

silver salt of *m*-nitrobenzsynaldoxime was prepared from pure *m*-nitrobenzsynaldoxime in the same way as the silver salt of 3:4-methylenedioxybenzantialdoxime above. An ethereal suspension of this salt was left in the dark for forty-eight hours with slightly less than the calculated quantity of ethyl chloroformate. After filtering and removing the ether, a crystalline product was obtained which was purified by placing it in a dry folded filter paper and pouring boiling benzene over it and collecting the filtrate in a cooled vessel, when *carbethoxy-m-nitrobenzsynaldoxime* was obtained as a white, crystalline powder melting at 138° (Found : N = 12.0. $\text{C}_{10}\text{H}_{10}\text{O}_5\text{N}_2$ requires N = 11.8 per cent.). When it was hydrolysed by heating for an hour with 2*N*-sodium hydroxide, ammonia was evolved; subsequent treatment with carbon dioxide gave no oxime, but acidifying with hydrochloric acid precipitated *m*-nitrobenzoic acid.

Carbethoxy-derivatives of p-Nitrobenzaldoxime.—These have been described by Dunn and one of us (*loc. cit.*). The results there obtained were, however, unique, so the preparation of these compounds was twice repeated and the previous results were fully confirmed. An attempt to prepare carbethoxy-*p*-nitrobenzsynaldoxime from the silver salt of *p*-nitrobenzsynaldoxime was frustrated owing to the hydrolysis of the sodium salt of the *syn*-oxime in aqueous solution and the consequent difficulty in preparing the silver salt therefrom.

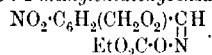
Carbethoxy-3-nitro-4-dimethylaminobenzantialdoxime,



—To a solution of 1 gram of 3-nitro-4-dimethylaminobenzantialdoxime in 20 c.c. of 2*N*-sodium hydroxide was added 0.5 gram of ethyl chloroformate. On shaking the mixture for some time, the *carbethoxy*-compound was precipitated as an orange-coloured solid, which crystallised from acetone and water in orange plates melting at 135° (Found : N = 14.8. $\text{C}_{12}\text{H}_{15}\text{O}_5\text{N}_3$ requires N = 14.9 per cent.). This compound was hydrolysed by heating on the water-bath with 2*N*-sodium hydroxide until solution was complete. During the process, a small amount of ammoniacal vapour was evolved. On saturating the alkaline solution with carbon dioxide, a copious precipitate of 3-nitro-4-dimethylaminobenzantialdoxime was obtained. After removing this, acidification of the solution with dilute hydrochloric acid gave a small precipitate of a compound which after crystallisation melted at 174–176° and appeared to be 3-nitro-4-hydroxybenzoic acid. As by far the greater portion of the

carbethoxy-derivative regenerated the original oxime, there is little doubt that the carbethoxy-compound had the *anti*-configuration.

Carbethoxy-6-nitro-3:4-methylenedioxybenzantialdoxime,



—This compound, prepared in an analogous manner to the above from 6-nitro-3:4-methylenedioxybenzantialdoxime, separates from the alkaline liquor as a faintly green solid, which crystallises from acetone and water in very pale yellow needles melting at 120° (Found: N = 10·2. $\text{C}_{11}\text{H}_{10}\text{O}_7\text{N}_2$ requires N = 10·0 per cent.). When this compound is warmed with 2*N*-sodium hydroxide, profound decomposition takes place as in the case of carbethoxy-*o*-nitrobenzsynaldoxime, but if the solid be left for some days in contact with 2*N*-sodium hydroxide at room temperature, hydrolysis will take place smoothly and carbon dioxide will precipitate from the solution the original oxime.

Action of Ethyl Chloroformate on Alkaline Solutions of syn-Alldoximes.—The *syn*-aldoximes were dissolved in 2*N*-sodium hydroxide and shaken with slightly less than the calculated quantity (1 mol.) of ethyl chloroformate, keeping the solutions cold. The product which separated, if solid, was filtered off or, if oily, extracted with ether, the ethereal solution dried with anhydrous sodium sulphate, and the solvent removed at room temperature. With the exception of the product from benzsynaldoxime, a solid was obtained by these methods which was crystallised from acetone and water. In all cases investigated, namely, benzsynaldoxime, *p*-chloro-, *o*-, *m*-, and *p*-nitro-, 3:4-methylenedioxy-, and *p*-methoxybenzsynaldoximes, the products obtained by the action of ethyl chloroformate proved to be the corresponding nitriles. In the case of benzonitrile, this was recognised by its odour and hydrolysis to benzoic acid and ammonia, whilst in the other cases the nitriles were identified by their melting points and mixed melting points with other specimens. When the alkaline solution of the *syn*-oxime was shaken with an ethereal solution of the ethyl chloroformate, whilst 3:4-methylenedioxy- and *p*-methoxy-benzsynaldoximes gave the corresponding carbethoxy-synaldoximes (see above), *m*- and *p*-nitrobenzsynaldoximes under the same conditions still gave the nitriles.

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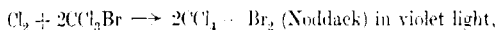
[Received, April 4th, 1923.]

CXXXVII.—*The Photochemistry of Unstable Substances.*

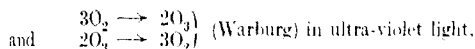
By EDMUND JOHN BOWEN.

AMONG the various attempts to apply the quantum theory to the problems of chemical reactivity is the so-called law of the photochemical equivalence, first obtained by Einstein (*Ann. Physik*, 1912, **37**, 832), which is generally accepted as forming a basis for the consideration of photochemical reactions. The number of molecules reacting is equated to the number of quanta in the light absorbed by the system. This law was shown by Einstein to be the necessary average (and approximate) result from the radiation laws in the case of a photochemical "stationary state" having properties of a rather hypothetical character. The view now taken is to regard the law as founded on the quantum absorption of radiant energy, and therefore as equally applicable to "irreversible" photochemical reactions.

In the case of actual photochemical reactions, the ratio quanta absorbed/molecules reacting assumes various values from ∞ to about 10^{-10} (compare Bodenstein, *Z. physikal. Chem.*, 1913, **85**, 329). Important investigations of the experimental validity of the law have been made by Warburg (summary, *Z. Elektrochem.*, 1920, **26**, 54), Henri and Würmser (*J. Phys. Radium*, 1913, [v], **3**, 305; *Compt. rend.*, 1913, **156**, 1012), and by Noddack (*Z. Elektrochem.*, 1921, **27**, 359). It appears that the law is closely followed in the reactions



and in the reactions



if readily acceptable assumptions are made as to a primary photochemical process followed by spontaneous secondary thermal reactions.

Deviations from unity of the measured ratio quanta absorbed/molecules reacting in other reactions are explained by Warburg and Nernst as due to three main causes:

- (1) The quantum absorbed may not be large enough to bring about the primary change.
- (2) The molecule may absorb a quantum, but may lose it again

by collision, the energy being degraded as heat ("deactivation by collision").

(3) Secondary spontaneous thermal reactions. Such reactions may form a chain, accounting for extraordinarily small values of the ratio (Nernst, *Z. Elektrochem.*, 1918, **24**, 335).

The first two causes make the ratio larger than unity; the third usually makes it smaller. So all actual cases are provided for.

In this investigation was studied the application of the law to the photochemical decomposition in violet light of carbon tetrachloride solutions of chlorine peroxide, chlorine monoxide, and nitrogen trichloride.

EXPERIMENTAL.

Materials.—The pure carbon tetrachloride of commerce was allowed to stand with chlorine peroxide, washed, dried with phosphoric oxide, and fractionally distilled.

Source of Light.—In order to reduce the necessary time of exposure of unstable solutions, an intense source of light is required. A carbon arc, taking 11 amperes at about 45 volts, with vertical, electromagnetically regulated negative electrode was used. The hand-fed positive electrode was horizontal, and was only 7 mm. in diameter to minimise wandering of the "spot." A permanent magnet deflected the arc so that the positive spot was situated at the extreme end of the electrode. With a condensing lens the light was concentrated on an aperture of area about 4 sq. cm., behind which the photochemical cell was placed. The blue and violet rays were isolated by means of trough filters containing solutions of ferrous ammonium sulphate and copper sulphate, and of crystal-violet.

The chief source of inaccuracy in the experiments was due to the fluctuations in the light intensity of the arc; this especially affected the absorption measurements. The inaccuracy on this account may reach 25 per cent.

Photochemical Cell.—A flat-walled cell was constructed, of internal width about 5 mm. and volume about 4.5 c.c., somewhat resembling a pyknometer in shape, and fitted with two taps lubricated with phosphoric acid. Filling was accomplished by forcing the solution through a capillary tip inserted through the bore of one of the taps. With this cell an accurately reproducible volume is employed at each filling, and the whole of the liquid can be removed for titration; auxiliary pipettes, involving exposure to air and loss of solute under the partial vacuum, are avoided; and loss of liquid during exposure is negligible.

Measurement of Energy.—The energy in the radiation employed was measured with a rough bolometer. A wide-angled cone of

about 20 ohms resistance, 2.5 cm. in diameter, was wound from 42-gauge silk-covered copper wire one layer thick, held together with a little shellac and blackened on the inside. The resistance change of this cone when heated by the radiation was measured against an approximately equal resistance composed of heavy-gauge manganin wire. It was calibrated by measuring its change of resistance when different amounts of electrical energy were expended in it. Three or four minutes were necessary for the instrument to come into equilibrium with the radiation.

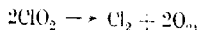
For the measurement of the energy absorbed in the various experiments a Melloni thermopile of 56 antimony-bismuth pairs was found convenient. Readings were made on a potentiometer wire connected in series with a suitable high resistance and an accumulator; the arrangement being calibrated by comparison with the bolometer.

The wave-lengths absorbed in these experiments reached from about 4100 Å. to 4700 Å. In calculating the number of quanta, a representative mean wave-length 4450 Å. has been employed; that is, $h\nu = 4.42 \times 10^{-12}$ erg.

Chlorine Peroxide Solutions.

Chlorine peroxide, prepared in an all-glass apparatus by warming at 60° a mixture of 8 grams of potassium chlorate, 30 grams of crystallised oxalic acid, and 4 c.c. of water (Bray, *Z. physikal. Chem.*, 1906, **54**, 463, 569, 731), was passed into carbon tetrachloride. The gas and the solutions were dried with phosphoric oxide. The solutions are bright yellow and show a characteristic absorption spectrum consisting of bands in the blue and the violet equally spaced on a frequency scale, with maxima at 4675, 4520, 4370, and 4220 Å. approximately. The bands are much fainter in the longer wave region. This spectrum resembles that found by Kåbitz (*Diss.*, Bonn, 1905) for the gas. The solutions decompose slowly in the dark, the rate of decomposition depending on the free space in the vessel above the liquid.

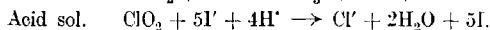
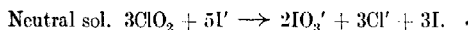
In light, the decomposition may be represented stoichiometrically



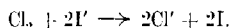
the oxygen largely remaining in the solution in a supersaturated condition.

Chlorine peroxide and chlorine in presence of one another were estimated by addition to excess of potassium iodide and titration with sodium thiosulphate, first with the solution neutral, and then acidified with dilute acid (Bray, *loc. cit.*).

The reactions are:



Chlorine reacts equally in neutral and acid solutions:



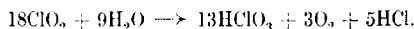
Summary of Results.—

Conc. of ClO_2 in gram-mol. per litre.	Molecules decomposed per sec. $\times 10^{-16}$.	Quanta per sec. in radiation $\times 10^{-19}$.	Mean absorp- tion.	Quanta absorbed Molecules decomposed
0.317	5.8	8.7	0.9	1.35
0.166	6.0	8.7	0.82	1.19
0.160	6.2	8.7	0.80	1.12
0.0945	5.03	8.7	0.74	1.28
0.0885	5.14	6.0	0.71	1.35
0.0856	4.75	8.7	0.70	1.28
0.0724	5.41	8.7	0.68	1.09
0.0622	4.47	8.7	0.67	1.28
0.0595	3.3	5.05	0.80	1.22
0.0585	5.2	8.7	0.65	1.09
0.0482	4.3	8.7	0.62	1.25
0.0346	4.41	8.7	0.57	1.12

In experiment 5, a yellow filter was employed to cut off the light of higher frequency.

The ratio quanta absorbed/molecules reacting was found to be independent of the light intensity over a range 1 to 6. It was also shown that an intermittent exposure produced the same effect as an equivalent continuous one.

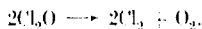
Chlorine peroxide dissolves in water to give a yellow solution which is photochemically sensitive. Popper (*Annalen*, 1885, **227**, 161; **231**, 137) has shown, however, that the decomposition in sunlight is complex, and has represented it by the equation



The reaction was therefore not studied.

Chlorine Monoxide Solutions.

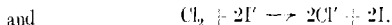
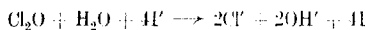
Gaseous chlorine monoxide was found to decompose slowly in light by its discoverer (Balard, *Ann. Chim. Phys.*, 1834, **57**, 225), although Garzarolli, Thurnlack, and Schackerl (*Annalen*, 1885, **230**, 273) reported only inappreciable decomposition after fifteen minutes' exposure to sunlight. Solutions of the gas in carbon tetrachloride undergo the stoichiometric decomposition in light



It was found unnecessary to prepare the gaseous substance. Dry solutions of chlorine in carbon tetrachloride react quickly and

quantitatively with yellow precipitated mercuric oxide to give brown solutions of chlorine monoxide. The absorption spectrum of the solutions consists of a broad indefinite band in the blue and violet, quite different from that of solutions of chlorine peroxide (compare results for the gases, Kayser, "Handbuch der Spectroscopie," 1905, Vol. III, p. 366).

The solutions were dried with phosphoric oxide before being used. Analysis was carried out by running the liquid into excess of potassium iodide solution, acidified with a known amount of standard acid, titrating the iodine liberated, and then titrating the excess of acid, using methyl-orange as an indicator. The reactions involved are

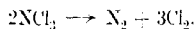


Summary of Results.—

Conc. of Cl_2O in gram-mol. per litre.	Molecules decomposed per sec. $\times 10^{-16}$.	Quanta per sec. in radiation $\times 10^{-16}$.	Mean absorp- tion.	Quanta absorbed Molecules decomposed.
0.145	4.4	8.7	0.60	1.18
0.140	4.03	8.7	0.585	1.24
0.134	4.91	8.7	0.55	0.98
0.112	4.14	8.7	0.49	1.03
0.110	4.04	8.7	0.48	1.04
0.109	3.55	8.7	0.47	1.15
0.0855	3.06	8.7	0.42	1.20

Nitrogen Trichloride Solutions.

Hentschel (*Ber.*, 1897, **30**, 1434) showed that nitrogen chloride, dissolved in various organic liquids, was decomposed by light, usually with formation of chlorination products of the liquids. In carbon tetrachloride, the decomposition is simple:



Solutions were prepared by shaking carbon tetrachloride containing chlorine with concentrated ammonium sulphate solutions, and were dried with phosphoric oxide. In colour, they resemble solutions of chlorine (Chapman, *T.*, 1909, **95**, 138). The light absorbed was small, making measurements inaccurate. Analyses according to the method of Dowell and Bray (*J. Amer. Chem. Soc.*, 1917, **39**, 896) yielded average ratios Cl/N of 3.5. The nitrogen chloride was estimated by running the solutions into concentrated sodium sulphite, and distilling off the ammonia into standard acid. The measurements are unsatisfactory because the amount of decomposition appeared only as a small difference.

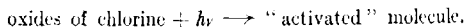
Summary of Results.—

Conc. of NCl_2 in gram-mol. per litre.	Molecules decomposed per sec. $\times 10^{-16}$.	Quanta per sec. in radiation $\times 10^{-16}$.	Mean absorp- tion.	Quanta absorbed Molecules decomposed
0.43	13.7	8.7	0.43	0.27
0.316	4.8	8.7	0.28	0.508
0.290	2.13	8.7	0.29	1.18
0.227	4.5	8.7	0.308	0.595

The results seem to indicate that more than one molecule is decomposed for each quantum absorbed.

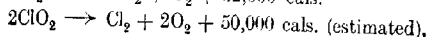
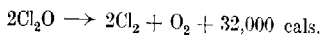
Discussion.

These results are of a preliminary character owing to the sources of error in the apparatus employed. They are, however, of sufficient accuracy to justify the raising of the question whether real unimolecular decompositions are ever found (compare Lowry, *Trans. Faraday Soc.*, 1922, 596). In the case of thermal reactions, it is remarkable that only two possibly unimolecular reactions in the gaseous state (where complications due to solvent cannot occur) are known; the decomposition of phosphine at high temperatures (Trautz and Bhandarkar, *Z. anorg. Chem.*, 1919, **106**, 95) and the decomposition of nitrogen pentoxide (Daniels and Johnston, *J. Amer. Chem. Soc.*, 1921, **43**, 53). Even in these cases the evidence is scarcely conclusive. The measurements with phosphine are extremely inaccurate, and the rigorous criterion of the effect of change of pressure does not seem to have been applied, whilst the unimolecular mechanism of the nitrogen pentoxide decomposition has been criticised by the investigators themselves (*J. Amer. Chem. Soc.*, 1922, **44**, 2402). Almost all photochemical reactions exhibit complications of varying degrees of obscurity, and the only guide is that radiant energy must be absorbed in quanta. It appears probable from the measurements in this paper that the photochemical decompositions of the oxides of chlorine are unimolecular, and that the views of Baly (see *Trans. Faraday Soc.*, 1922, 588) and of Weigert (*Z. physikal. Chem.*, 1922, **102**, 416) are unnecessary for the explanation of these cases. The mechanism of the decomposition may be formulated

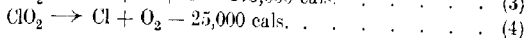
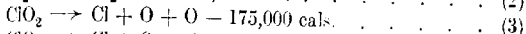
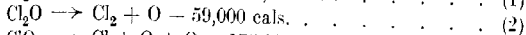
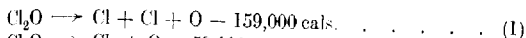


These "activated" molecules then largely decompose by a "dark" reaction. If this is so, then the unimolecular decomposition of the "activated" molecule would be expected to *evolve* heat; and this enables the mechanism to be discussed. The energy in violet light corresponds with 65,000 cal. per gram-molecule. The other

heat data available are only very approximate, and apply to the gaseous substances. In the dissolved state, the unknown heats of solution must be reckoned with, but it is unlikely that these will be large enough to invalidate the general results of the reasoning. Taking as rough approximations

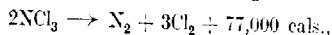


and the heats of dissociation of chlorine and oxygen as 100,000 cal. and 150,000 cal., respectively, we obtain for the hypothetical thermal reactions

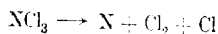


The only reactions possible to a molecule activated to the extent of 65,000 cal. are (2) and (4).

In the case of the decomposition of nitrogen trichloride, taking



even the reaction



is not possible in violet light if the heat of dissociation of nitrogen is more than 110,000 cal., as is probable. The assumption that this decomposition is not unimolecular, but that the activated molecule attacks an unactivated one, would agree with the rather unsatisfactory experimental results so far obtained. This reaction is being further studied.

The results obtained in this investigation are not considered sufficiently precise to say whether in obtaining the ratio quanta absorbed/molecules reacting the energy should be calculated in quanta at the frequencies actually absorbed, as appears probable, or at the frequency of the head of the band, as has been suggested (Lewis, "Physical Chemistry," 1919, Vol. III, p. 137).

If the constant frequency difference bands in the absorption spectrum of chlorine peroxide solutions are due to the superposition of rotational quanta on a vibrational quantum, such a decision would throw light on the interchanges between the various kinds of energy within the molecule.

Summary.

1. The photochemical decomposition of carbon tetrachloride solutions of chlorine peroxide and of chlorine monoxide under the

influence of violet light appears to agree with the law of the photochemical equivalence. Solutions of nitrogen trichloride in similar circumstances give less certain results not far removed from the requirements of the law.

2. The mechanism of the photochemical decomposition has been discussed.

The thanks of the author are due to the Research Fund Committee of the Chemical Society for a grant which partly defrayed the expenses of the work.

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[Received, March 13th, 1923.]

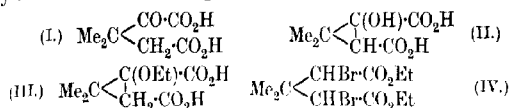
CXXXVIII.—*Ring-chain Tautomerism. Part V. The Effect of the gem-Dipropyl Grouping on the Carbon Tetrahedral Angle.*

By LESLIE BAINS and JOCELYN FIELD THORPE.

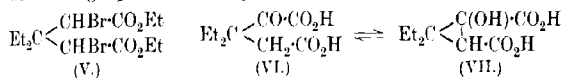
WHEN, as described in Part II of this series (T., 1922, **121**, 1436), it was discovered that the *gem*-diethyl group ($\text{Et}_2\text{C}<$) exerted an influence on the carbon tetrahedral angle which was quite different in effect from that exercised by the *gem*-dimethyl group ($\text{Me}_2\text{C}<$), it was evident that it would be necessary to prepare as many $\beta\beta$ -dialkylglutaric acids as possible and to compare their behaviour under similar conditions, in order to ascertain the cause of this wholly unexpected result. If the difference in effect were due to a difference in volume between the dimethyl and diethyl groupings, it would mean that this influence would have to be exerted through the single carbon atom by which, in the case of ethyl, the groups are attached to the β -carbon atom, or, in other words, we should have to assume that the volume effect of the attached carbon atom is affected by its participation in a chain of carbon atoms of which it is a member. If this assumption is true, it is to be expected that an increase in the length of the chain of which the *gem*-grouping is composed will exert a corresponding influence on the value of the angle formed by the two remaining valencies of the β -carbon atom and that this influence could be detected by the stability of the ring structures or open-chain compounds derived from the substituted acids in question.

It will be remembered that the influence of the *gem*-dimethyl group conferred stability on the open-chain keto-compound (I)

and that it was apparently impossible to obtain the isomeric ring compound (II), although derivatives of this form (III) were obtained by the action of alcoholic potash on the dibromo-ester (IV):



On the other hand, the action of alcoholic potash on the dibromo-ester (V) in the *gem*-diethyl series did not lead to the formation of any alkyloxy-derivative of type (III), but to a mixture of the keto-acid (VI) and the hydroxy-ring acid (VII); the two compounds being subsequently found to be tautomeric in the sense that they each formed the same equilibrium mixture containing 38 per cent. of the keto-acid and 62 per cent. of the ring acid, when treated with strong aqueous caustic potash.



An investigation of the intermediate methyl ethyl derivatives $\left(\begin{smallmatrix} \text{Et} \\ \text{Me} \end{smallmatrix} > \text{C} \right)$ (this vol., p. 113) led to a discovery which revealed the cause of the formation of the alkyloxy-derivative, for it was found that the alkyloxy-ring compound, which was formed in this instance just as in the *gem*-dimethyl series, could be hydrolysed by hydriodic acid completely to the keto-acid.

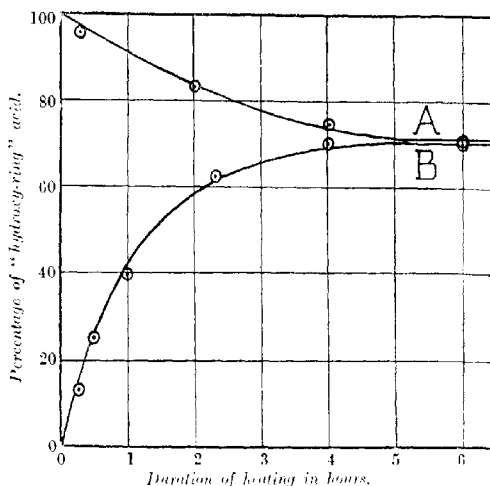
Since then it has been shown by Mr. Balbir Singh, working in these laboratories, that the same reaction is also characteristic of the dimethyl derivative and that the action of dilute hydrobromic acid on the alkyloxy-compound leads to a quantitative formation of the keto-acid. These experiments prove, therefore, conclusively that the ring-hydroxy-form is unstable in the dimethyl and methyl ethyl series and that it passes at the moment of its formation into the open-chain isomeric keto-acid. The first evidence of the stability of the ring structure is obtained in the diethyl series, where the two isomeric compounds, the open-chain keto-acid and the hydroxy-ring acid, are tautomeric.

The present paper deals with the first of the series of investigations on the influence of radicles higher in the paraffin series, and contains the work which has been carried out with 3,3-di-*n*-propylglutaric acid.

3,3-Di-*n*-propylglutaric acid was prepared by Kon's modification (L. 1921, 119, 818) of Guareschi's reaction. It was characterised by the formation of the anhydride and anilic acid, two well-defined

crystalline substances which were not prepared by Guareschi and which are admirably adapted for the purposes of identification. The acid can be readily converted by the usual methods into the $\alpha\alpha'$ -dibromo-ester (VIII), which on distillation passes into the bromo-lactone ester (IX). The corresponding dibromo-acid (X)

FIG. 1.

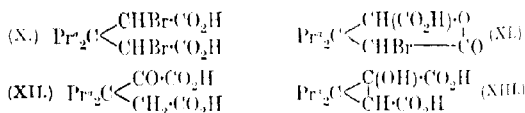


A. Conversion of "hydroxy-" to "keto-" acid.
B. Conversion of "keto-" to "hydroxy-" acid.

and the bromo-lactonic acid (XI) were also prepared by the usual methods:



From the dibromo-ester a mixture of the keto-acid (XII) and the hydroxy-ring acid (XIII) was obtained.



The determination of the equilibrium mixture between these two substances in 60 per cent. aqueous potash gave the ratio (see curve) of 71 : 29 in favour of the hydroxy-ring. The ratio is, therefore, appreciably higher than the 62 : 38 found for the diethyl derivatives.

This is in accordance with the view that the increase in the number of carbon atoms in the chain forming the *gem*-grouping increases the stability of a three-membered ring system formed by the other two valencies. Further and quite remarkable evidence was obtained on this point during these investigations, and this will form the subject of another communication in the near future.

EXPERIMENTAL.

Condensation of Di-n-propyl Ketone with Cyanoacetic Ester and Ammonia. Preparation of $\alpha\gamma$ -Dicyno- $\beta\beta$ -di-n-propylglutarimide and $\beta\beta$ -Di-n-propylglutaric Acid.

It was found that a considerable economy could be made in the proportion of cyanoacetic ester used in this condensation without any detriment to the yield of the imide.

Five hundred c.c. of absolute alcohol, cooled in a very efficient freezing mixture, were saturated with ammonia and added to a mixture of 143 grams ($1\frac{1}{2}$ mols.) of dipropyl ketone and 180 c.c. ($1\frac{1}{2}$ mols.) of cyanoacetic ester at 0° . The solution, having been kept at room temperature for a fortnight, was diluted with 2 litres of water, extracted five times with ether, and a very small quantity of a substance insoluble both in water and ether removed by filtration. From the ethereal solution, after washing with water, drying over calcium chloride, and removal of the ether through a fractionating column, 100 grams of unchanged ketone were recovered. The aqueous solution on acidification with hydrochloric acid deposited the imide in minute, colourless prisms, which were kept twenty-four hours before filtering. The yield was only 30 grams, but from the mother-liquors on evaporation to dryness and extraction with water a further 2–3 grams were obtained.

Thirty grams of this crude imide were hydrolysed by boiling with 800 c.c. of 60 per cent. (by weight) sulphuric acid for four hours (compare Guareschi, *Gazzetta*, 1919, **49**, i, 124). The imide slowly passed into solution with decomposition and frothing and evolution of carbon dioxide, and after one and a half hours the molten acid began to separate on the surface of the boiling mixture. On the completion of the reaction the whole was poured into a large volume of water, when the acid was precipitated in a colourless, pure, crystalline condition: the yield was 93.5 per cent. of theory.

$\beta\beta$ -Di-n-propylglutaric acid is very sparingly soluble in ether or cold water, but dissolves readily in hot benzene and in boiling water, and separates from the latter solvent in lustrous, white, pearly flakes which felt together. It melts at 114.5 – 115° (Guareschi, *loc. cit.*, gives 112 – 113°) (Found: C = 61.0; H = 9.4. Calc., C = 61.1; H = 9.3 per cent.).

The *anhydride* was prepared by boiling the acid under reflux for three hours with excess of acetyl chloride. This was removed in a partial vacuum and the residue distilled under diminished pressure. It boiled at 173—174°/12 mm. and when cooled solidified in large, fern-like, colourless crystals melting at 24—25°. It is very stable, apparently more so than the anhydrides of dimethyl- and trimethylglutaric acids, and is only reconverted to the acid by boiling with water for several hours (Found: C = 66·3; H = 9·2. $C_{11}H_{18}O_3$ requires C = 66·6; H = 9·2 per cent.).

The *anilic acid*, prepared by mixing cold benzene solutions of the anhydride and aniline, and crystallising the precipitated product from 84 per cent. alcohol, forms colourless, stumpy, prismatic crystals which melt at 160—161° (Found: C = 70·0; H = 8·7. $C_{17}H_{25}O_3N$ requires C = 70·0; H = 8·7 per cent.).

Dibromination of $\beta\beta$ -Di-n-propylglutaric Acid.

$\alpha\alpha'$ -Dibromo- $\beta\beta$ -di-n-propylglutaric Acid.—21·6 Grams of the acid were treated with 41·7 grams of phosphorus pentachloride (2 mols.) and warmed on the steam-bath until evolution of hydrogen chloride ceased (one-half to three-quarters of an hour). To this liquid, 13·3 c.c. of bromine (2·4 mols.) were added in small quantities during three hours, and the mixture was kept on the steam-bath for fifteen hours. The product was poured into 150 c.c. of well-cooled absolute alcohol, and after being kept for twenty-four hours was treated with water and the precipitated oil extracted with ether. The ethereal solution was washed with dilute sodium carbonate to remove the traces of acidic products present and dried over fused calcium chloride. On removing the ether, the crude dibromo-ester remained as a golden-yellow oil of about 80 per cent. purity, which could not be further purified, as it readily decomposed into its bromo-lactone on distillation under diminished pressure (Found: Br = 32·9. $C_{13}H_{26}O_4Br_2$ requires Br = 37·1 per cent.).

Lactone of Ethyl Hydrogen α -Bromo- α' -hydroxy- $\beta\beta$ -di-propylglutarate (IX).—The production of this substance in an almost quantitative yield by the distillation under reduced pressure of the crude dibromo-ester establishes the constitution of the latter. The bromo-lactonic ester is a colourless, exceedingly viscous oil which shows no tendency to crystallise, and is presumably a mixture of the *cis*- and *trans*-modifications. It boils at 190—191°/15 mm. (Found: C = 48·9; H = 6·8; Br = 25·0, 24·9. $C_{13}H_{21}O_4Br$ requires C = 48·6; H = 6·6; Br = 24·9 per cent.).

Acid Ester.—The sodium carbonate washings from the neutral ester, when acidified and extracted with ether, yielded a very

small quantity of the monobromo-acid ester : much larger quantities were obtained when thionyl chloride was substituted for phosphorus pentachloride. It could not be distilled without decomposition, and the crude liquid was analysed after keeping in a vacuum over potash for some days (Found : Br = 24.8. $C_{13}H_{23}O_4Br$ requires Br = 24.7 per cent.).

αα'-Dibromo-ββ-di-n-propylglutaric Acid (X).—The crude dibromination product, prepared as before, was poured into anhydrous formic acid instead of into alcohol, and the solution was warmed on the steam-bath until all effervescence ceased (two hours), and allowed to evaporate spontaneously at the ordinary temperature. After three days, the semi-solid precipitate was separated and the gummy contamination removed from it by washing with a small quantity of a mixture of chloroform and petrol (b. p. 40–60°). The remaining brown, granular solid was purified by alternate crystallisation from benzene and washing with a chloroform–light petroleum mixture. The pure acid is almost insoluble in cold benzene and crystallises in small, dense, colourless prisms, which soften at 145° and melt with decomposition at about 155° (Found : C = 35.2; H = 4.9. $C_{11}H_{19}O_4Br_2$ requires C = 35.3; H = 4.9 per cent.).

Lactone of α-Bromo-α'-hydroxy-ββ-di-n-propylglutaric Acid (XI).—The dibromo-acid was readily converted into the bromo-lactonic acid by loss of hydrogen bromide. The acid was dissolved in glacial acetic acid and warmed for a few minutes. The addition of water precipitated an oil which solidified on keeping; it was drained on porous plate and crystallised from benzene, when it formed small, colourless prisms melting at 135–136° (Found : Br = 27.3. $C_{11}H_{17}O_4Br$ requires Br = 27.3 per cent.).

Hydrolysis of the Bromo-lactonic Ester (IX). Formation of α-Keto-ββ-di-n-propylglutaric Acid (XII) and 3:3-Di-n-propylcyclopropan-1-ol-1:2-dicarboxylic Acid (XIII).

The hydrolysis of the bromo-lactonic ester was carried out under different conditions, the strength of the potash being varied from 10 to 80 per cent. and the duration of heating from two minutes to half an hour. The products of the reaction were mainly the open-chain keto-acid together with a small quantity of the isomeric hydroxy-ring acid and traces of oxalic acid, the proportion of the last two becoming slightly greater with the higher concentrations of potash.

α-Keto-ββ-di-n-propylglutaric Acid (XII).—The crude keto-acid was obtained as follows in an 80 per cent. yield together with 7 per cent. of the hydroxy-acid. Five grams of the bromo-lactonic

ester were added as rapidly as possible to a boiling 43 per cent. aqueous potash solution (15 grams of KOH in 20 c.c. of water) and the heating was continued for two minutes. The solution was diluted, extracted with ether to ensure the purity of the product, acidified with hydrochloric acid, and cooled to 0° , when a small quantity (0.2 to 0.3 gram) of the hydroxy-ring acid was precipitated. The ethereal extract of the filtered solution, after drying over sodium sulphate and removal of the solvent, left 2.9 grams of an oil which became solid in the course of two days. It was drained from adherent oil on unglazed tile and crystallised from hot benzene, when 1.4 grams of the pure keto-acid were obtained.

α -Keto- $\beta\beta$ -di-*n*-propylglutaric acid is very soluble in hot benzene and separates slowly on cooling in small, prismatic crystals which are very dense and hard and melt at 104 – 104.5° . It is only sparingly soluble in light petroleum, but dissolves readily in ether, acetone, or water (Found: C = 57.25; H = 7.9; equivalent, by titration with baryta, = 114.4. $C_{11}H_{18}O_5$ requires C = 57.35; H = 7.9 per cent.; equivalent = 115).

Its semicarbazone is precipitated when warm aqueous solutions of the acid, semicarbazide hydrochloride, and sodium acetate are mixed, and after recrystallisation from dilute alcohol melts at 184° . The acid can be quantitatively regenerated from it by very careful treatment with warm dilute hydrochloric acid or by boiling with 20 per cent. oxalic acid for three-quarters of an hour (Found: N = 14.8. $C_{12}H_{21}O_5N_3$ requires N = 14.6 per cent.).

3 : 3-Di-*n*-propylcyclopropan-1- α -1 : 2-dicarboxylic Acid (XIII).—This was obtained in small quantity when the bromo-lactonic ester was hydrolysed with 64 or 80 per cent. aqueous potash, and was also produced by the action of methyl alcoholic potash (30 per cent.) on the dibromo-ester, but it was best prepared from the keto-acid by prolonged boiling with 60 per cent. potash (see below). It is sparingly soluble in boiling water and insoluble in cold water, dry ether, or hot benzene, but dissolves in acetone. It crystallises from a large volume of water (1 gram of acid in 100 c.c. of water) in colourless plates having a pearly lustre, and melts at 214° . Its ammonium salt is decomposed by boiling with water (Found: C = 57.2; H = 7.9; *M* (dibasic) by titration = 235. $C_{11}H_{18}O_5$ requires C = 57.35; H = 7.9 per cent.; *M* = 230).

Just as in the cases of the analogous hydroxy-ring acids from diethylglutaric acid (T., 1922, 121, 1440) and cyclohexane-1:1-diacetic acid (T., 1915, 107, 1080), and indeed cyclopropanol-1:2-dicarboxylic acid itself (T., 1921, 119, 305), this acid has so far resisted all attempts to acetylate it, and in particular was recovered unchanged after several hours' heating at 100° with acetyl chloride.

Equilibrium Mixture.—A tautomeric equilibrium between the salts of the keto- and hydroxy-acids is very slowly attained in the presence of 60 per cent. aqueous potash, and more rapidly, although with much decomposition, with 77 per cent. potash. In the latter case, the potassium salts of the acids separate as an oil on the surface of the boiling potash, and therefore a true equilibrium determined by the relative stability of the keto- and hydroxy-forms is not established, and the ratio of these two isomerides in the product, which contains approximately 50 per cent. of each, is governed by the solubilities of their respective potassium salts. Consequently, the tautomeric change had to be effected in 60 per cent. potash.

Either of the pure acids was boiled under reflux with a large excess of 60 per cent. aqueous potash for different periods of time varying from fifteen minutes to six hours. The hydroxy-ring acid, which was quantitatively precipitated from the diluted solution on acidification and cooling to 0°, was collected, dried, and weighed. The keto-acid was recovered from the filtrate by six extractions with ether, the crystalline solid left on evaporation of this solvent dissolved in a little water and treated with a slight excess of an aqueous solution of semicarbazide hydrochloride and sodium acetate, and the precipitated semicarbazone collected, dried, and weighed. The following table and the graph show that the equilibrium between the potassium salts of the two acids is established only after about four and a quarter hours' boiling, but that further heating has no effect on it, and that the same final mixture, containing approximately 29 per cent. of the keto-form, is reached from either side. The reaction is a truly unimolecular one, as the time-log. concentration curve plotted from these figures is approximately linear.

Hydroxy-ring Acid :

Initial acid (grams).	Time (hours).	Grams of recovered				Percentage, Hydroxy-acid : keto-acid.
		Semi-carbazone.	Equivalent to keto-acid.	Hydroxy-acid.	Total.	
1.9	1	0.10	0.08	1.55	1.63	95 : 5
1.0	2	0.18	0.14	0.70	0.84	83 : 17
1.0	4	0.26	0.21	0.63	0.84	75 : 25
1.0	6	0.33	0.26	0.63	0.89	71 : 29

Keto-Acid :

2.0	1	2.02	1.62	0.25	1.87	13 : 87
1.8	1	1.50	1.20	0.40	1.60	25 : 75
0.5	1	0.25	0.20	0.13	0.33	39 : 61
2.0	21	0.89	0.71	1.20	1.91	63 : 37
1.0	4	0.30	0.24	0.57	0.81	70 : 30
1.0	6	0.30	0.24	0.58	0.82	71 : 29

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T T

The authors desire to express their thanks to the Royal Society for a grant which has defrayed the expense of this research, and one of them (L. B.) also acknowledges his indebtedness to the Department of Scientific and Industrial Research for a grant which has enabled him to participate in the work.

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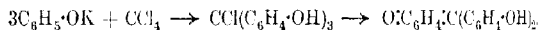
[Received, April 17th, 1923.]

CCXXXIX.—*Dyes of the Aurin Type. Part I.*

By HARRY BAINES and JOHN EDMUND DRIVER.

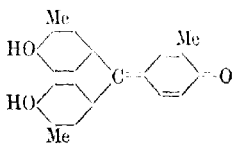
THIS investigation arose out of an attempt to elucidate the mechanism of the Reimer-Tiemann reaction. It was thought possible that during the action of chloroform or carbon tetrachloride on alkaline solutions of phenol ω -chloroanisoles are formed as intermediate products, and in attempts to isolate them dry sodium phenoxide was subjected to the action of chloroform or carbon tetrachloride. Owing to the nature of the results of preliminary experiments, the action of chloroform and of carbon tetrachloride on various metallic derivatives of phenols and naphthols was studied.

This communication deals with the action of carbon tetrachloride on derivatives of phenol and of the cresols. From phenol, aurin is produced, whilst *o*- and *m*-cresols yield the corresponding trimethylaurins (I and II), the carbon tetrachloride providing the nuclear carbon atom; for example,

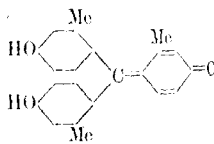


The velocity of the reaction was found to depend largely on the temperature, and, in the case of phenol, on the nature of the metallic derivative employed.

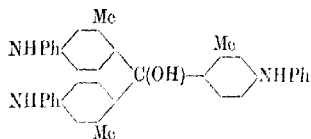
The 2:2':2''- and 3:3':3''-trimethylaurins have not been previously described. They are red, crystalline compounds, very similar to aurin itself. 2:2':2''-Trimethylaurin gives a compound (III) similar to aniline-blue when heated with aniline and acetic acid, but no such derivative could be prepared from 3:3':3''-trimethylaurin, probably owing to the effect of steric hindrance produced by the methyl groups on the adjacent hydroxyl groups.



3:3':3''-Trimethylaurin (I.)



2:2':2''-Trimethylaurin (II.)



NN',N'',Triphenyl-2:2':2''-trimethylparaosaniline (III.)

In the case of *p*-cresol, no trimethylaurin was produced. A *p*-"kresolaurin" has been described by Nencki (*J. pr. Chem.*, 1882, [iii], 25, 275), but on repeating Nencki's experiments a product was obtained quite different in properties from that described by him. Indeed, the existence of a compound of the aurin type derived from *p*-cresol seems highly improbable, since the para-position to the hydroxyl group is already occupied, and therefore such a derivative could not have a para-quinonoid structure.

The earlier investigators (Dale and Schorlemmer, *this Journal*, 1871, 24, 466, *et seq.*; Kopfer, *ibid.*, 1876, i, 660; Erhart, *Arch. Pharm.*, 1876, [iii], 8, 481; Zulkowski, *Ber.*, 1878, 11, 391; Gukasianz, *ibid.*, p. 1179) obtained widely differing results in the analysis of aurin, the values recorded for carbon varying between 61 and 80 per cent. This was apparently largely due to the tenacity with which crystalline aurin retains water and acetic acid. The results recorded in the present paper for the analysis of aurin and of the trimethylaurins were obtained with samples dried at 150–160° during many hours (compare Dale and Schorlemmer, *this Journal*, 1873, 26, 434; and Kopfer, *loc. cit.*).

Carbon tetrachloride has previously been employed in the synthesis of triphenylmethane and some of its derivatives (Friedel and Crafts, *Compt. rend.*, 1877, 84, 1453; E. and O. Fischer, *Annalen*, 1878, 194, 254; Gomberg, *Ber.*, 1900, 33, 3144; Heumann, D.R.-P. 68976, *Frdl.*, III, 103). In all these cases, the Friedel-Crafts' method, or a modification of it, was employed, aluminium chloride or zinc chloride being used as a condensing agent.

The action of chloroform and of carbon tetrachloride on other metallic derivatives of phenols and naphthols is at present under investigation, and interesting results have already been obtained.

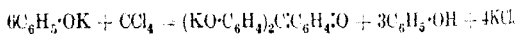
EXPERIMENTAL.

Potassium phenoxide was prepared by mixing aqueous solutions of phenol and potassium hydroxide in molecular proportions and evaporating to dryness, care being taken not to allow the temperature to rise above 170°. Sodium and calcium phenoxides were prepared in a similar manner. The potassium tolyloxides could

not be obtained pure by this method, since at the temperature required for the complete removal of the water, some decomposition of the tolyloxides took place. They were therefore made by mixing alcoholic solutions of potassium hydroxide and the required cresol in molecular proportions and evaporating off the alcohol at 110° under diminished pressure. In this way, the tolyloxides were obtained in colourless, deliquescent crystals, which could be heated at 140° without decomposition.

Action of Carbon Tetrachloride on Potassium Phenoxide.—When dry potassium phenoxide was boiled with excess of carbon tetrachloride during eight hours, although the solution turned a deep red, there was very little reaction. This was also the case when experiments were conducted during times varying from eight to thirty-six hours, pyridine or finely divided copper being used as catalyst.

Potassium phenoxide heated at 170° in a stream of carbon tetrachloride vapour during three to four hours gave a dark-coloured product, which, when extracted several times with carbon tetrachloride, yielded some phenol. The dark residue, when treated with water, dissolved, forming a deep red solution containing a considerable amount of potassium chloride. On diluting and acidifying with hydrochloric acid, a bulky, orange precipitate formed and more phenol was liberated. After removing the phenol by steam distillation, the orange solid was collected, washed, and dried. The product was a brick-red powder, which separated from a mixture of alcohol and glacial acetic acid in small crystals with a beetle-green lustre, and crystallised well in fine, red needles from brine acidified with hydrochloric acid. It was identified as aurin by its physical and chemical properties, including the study of its absorption spectrum in alkaline solution, and by the preparation of *N,N'*-triphenylpararosaniline by heating it with aniline and glacial acetic acid (Found: C = 78.60; H = 4.66. Calc., C = 78.61; H = 4.83 per cent.). Eighteen grams of potassium phenoxide yielded 59 grams of aurin. Since the aurin is produced in the form of its potassium derivative and a considerable amount of free phenol is formed, the reaction probably takes place as follows:



Calculated from this equation, the yield of aurin is 75 per cent. of the theoretical. An attempt was made to prevent the formation of phenol, and thus to increase the yield of aurin, by using an intimate mixture of potassium hydroxide and potassium phenoxide in molecular proportions. In this case, only a trace of aurin was formed, the product consisting mainly of unchanged potassium

hydroxide and potassium phenoxide together with some potassium chloride and potassium carbonate.

Action of Carbon Tetrachloride on Sodium and Calcium Phenoxides.

—With sodium or calcium phenoxide, as with potassium phenoxide, very little reaction took place at the boiling point of carbon tetrachloride, even when pyridine or finely divided copper was used as catalyst. By the action of carbon tetrachloride vapour on sodium or calcium phenoxide at 170–190°, aurin was produced, but the reaction was very slow, as the following comparative yields indicate :

Time four hours.	Yield of aurin per 100 grams of phenol.
Potassium phenoxide	40 grams
Sodium "	9 "
Calcium "	3 "

3:3':3''-Trimethylaurin (Formula I).—Carbon tetrachloride vapour was passed over potassium *o*-tolylxide, heated at 110° during five hours, and the product was isolated as in the case of aurin. It was a brick-red powder sparingly soluble in water, the aqueous solution being pale yellow. It dissolved readily in alkalis, forming a deep red solution, and separated as a flocculent, orange precipitate on acidifying with hydrochloric acid. It dissolved readily in glacial acetic acid and in alcohol, but was crystallised with difficulty from these solvents. It was purified by recrystallisation from 10 per cent. hydrochloric acid, being obtained in tufts of fine, red needles (Found: C = 79.62; H = 6.11. $C_{22}H_{20}O_3$ requires C = 79.50; H = 6.03 per cent.).

2:2':2''-Trimethylaurin (Formula II).—This compound was obtained by the action of carbon tetrachloride vapour on potassium *m*-tolylxide at 110°. It was a red powder, sparingly soluble in water, forming a pale pink solution, and readily soluble in alcohol and in glacial acetic acid. It dissolved freely in alkalis, forming a deep red solution, but a dilute alkaline solution appeared slightly purple when compared with alkaline solutions of aurin or of 3:3':3''-trimethylaurin of similar strength. It was purified by crystallisation from 10 per cent. hydrochloric acid, being thus obtained in small, red needles (Found: C = 79.12; H = 6.09. $C_{22}H_{20}O_3$ requires C = 79.50; H = 6.03 per cent.). The compound resembled aurin very closely in physical and chemical properties. Thus, by treating a solution of it in glacial acetic acid with a slight excess of bromine, a bromo-derivative was obtained which dissolved in alkalis, forming a deep violet solution.

XXN"-Triphenyl-2:2':2''-trimethylpararosaniline (Formula III).—2:2':2''-Trimethylaurin (1 gram) was boiled with aniline (5 grams) and glacial acetic acid (2 grams) during forty-eight hours.

The blue liquid was poured into sodium hydroxide solution, and after boiling for one hour the excess of aniline was separated by distillation in a current of steam. The almost black solid was filtered off and washed well with boiling water to remove any unchanged acetanilide. The compound is insoluble in water, but dissolves readily in alcohol, from which it separates by evaporation in the cold in very small, dark blue crystals. The hot alcoholic solution is of a deep claret colour, but, on cooling, the colour changes to a pure deep blue. The base is somewhat soluble in hydrochloric and in sulphuric acids, forming deep blue salts. After drying the compound at 120° , the nitrogen was estimated by the Kjeldahl method (Found: N = 7.41. $C_{20}H_{13}ON_3$ requires N = 7.30 per cent.).

Action of Carbon Tetrachloride on Potassium p-Tolyloxide.—Potassium *p*-tolyloxide was heated at 110° in a stream of carbon tetrachloride vapour, and the product isolated as before. It was a light grey, amorphous powder forming a slightly brown solution in aqueous sodium hydroxide. The substance is being further investigated with the view of establishing its constitution.

Action of Formic Acid on p-Cresol in the Presence of Zinc Chloride.—This was a repetition of Nencki's preparation of the so-called "Kresolaurin" (*loc. cit.*).

Pure *p*-cresol (20 grams) was heated with anhydrous formic acid (10 grams) and anhydrous zinc chloride (25 grams) at 105 – 110° during one hour. A viscous, brown syrup was obtained. The product, when isolated, was a light grey, amorphous powder similar to that obtained by the action of carbon tetrachloride on potassium *p*-tolyloxide, and, like the latter, it was soluble in aqueous potassium hydroxide, forming an exactly similar pale brown solution. Nencki, however, describes "Kresolaurin" as a red, amorphous powder, insoluble in water but readily soluble in alkalis, giving a fuchsine-red solution. It seems probable that Nencki's product was simply the substance described above mixed with aurins, which would have been formed if impure *p*-cresol, containing phenol and other cresols, had been used.

The authors wish to express their thanks to Professor F. S. Kipping, F.R.S., for the kind interest he has taken in this research. One of us (H. B.) is indebted to the Department of Scientific and Industrial Research for a grant which has enabled a part of this work to be carried out.

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[Received, March 17th, 1925.]

CXL.—*Some Factors Governing the Complete Sorption of Iodine by Carbon from Chloroform Solution.*

By JAMES BRIERLEY FIRTH and FRED SHEASBY WATSON.

IN the majority of investigations on the sorption by carbon of a substance from solution the main object has been to determine the distribution of the solute between the carbon and the liquid solvent under conditions such that the solute is present throughout, in both the carbon and liquid solvent.

In a previous investigation by one of us (Firth, *Trans. Faraday Soc.*, 1921, **16**, 434), it was shown that, using $N/10$ -solutions of iodine in chloroform and benzene, the whole of the iodine was not sorbed by the carbon after a period of five years, even when the carbon used was as much as 8 grams per 100 c.c. of solution. It was shown that the concentration of the iodine in the liquid solvent diminished rapidly to a very low value in the case of active carbons such as lampblack, sugar carbon, and blood charcoal; after which the change in concentration was only very small, even over very long periods. In several cases, about 90 per cent. of the dissolved iodine was taken up by the carbon within twenty-four hours, using 4 grams of carbon per 100 c.c. of solution, yet in no case, even with carbon up to 8 grams per 100 c.c. of solution, was complete bleaching obtained.

In the present investigation, the object was to determine some of the conditions for the complete transference of the iodine from the chloroform solution to the sorbing carbon, that is, conditions for complete bleaching.

EXPERIMENTAL.

The chloroform was dried for several days over calcium chloride, then fractionated, the first and the last runnings being rejected. The carbon was sugar carbon as supplied by Merck, and gave less than 0.1 per cent. of ash. Solutions of pure resublimed iodine were prepared of strengths $N/1000$ and $N/100$, and in certain cases $N/10$.

The carbon was finely pulverised, and activated as hereafter described. The approximate densities of the various specimens of the carbon were determined by the water displacement method. All experiments were carried out at 18°. The carbon was weighed out into well-stoppered flasks of 50 c.c. capacity, 25 c.c. of the iodine solution were rapidly added, and the contents shaken. After definite intervals, the carbon was allowed to settle, the liquid rapidly decanted off, and 10 c.c. of the solution were transferred to

a stoppered bottle and titrated with standard sodium thiosulphate; usually $N/1000$ -thiosulphate was employed; but in some cases it was necessary to use $N/2000$. The intervals of exposure of the carbon were gradually increased until a point was reached at which the whole of the iodine had been taken up by the carbon, that is, there was no detectable iodine in the chloroform.

The results are expressed throughout in terms of 100 c.c. of solution; m is the number of grams of carbon per 100 c.c. of solution; x/m the number of grams of iodine per gram of carbon; and $a-x$ the final concentration of the solution in grams per 100 c.c. The results recorded in the present paper are typical, and indicate the fundamental points of some three hundred experiments.

First Series.—The object of this series was to determine the time required for complete bleaching by carbons which had been subjected to various treatments, namely,

(a) The carbon as received was finely powdered and heated at 100° for three hours.

(b) The carbon as received was finely powdered, heated in a quartz flask at about 600° in a vacuum for two hours, and allowed to cool in a vacuum.

(c) The carbon as received was finely powdered, heated in a quartz flask at about 900° in a vacuum for two hours, and allowed to cool in a vacuum.

(d) The carbon (b), after treatment with iodine solution, was collected and heated at a moderate temperature in an open dish until the whole of the iodine had been expelled. The carbon was then digested several times with alcoholic potash and repeatedly boiled with distilled water until the extract gave no opalescence with silver nitrate solution. It was then dried and heated in a vacuum at 600° , as in (b).

The densities of the carbons after the above treatment were 1.63, 1.64, 1.68, and 1.70, respectively.

Results.—

Carbon (a)	$\left\{ \begin{array}{l} m = 4, \\ \text{Iodine } \left\{ \begin{array}{l} \text{solution } \left\{ \begin{array}{l} N/1000, \end{array} \right. \end{array} \right. \end{array} \right.$	Time = 24 hours.	$x/m = 0.001175$;	$a - x = 0.008$.
		15 days.	$x/m = 0.00155$;	$a - x = 0.0065$.
Time required for complete bleaching.				
Carbon (b)	$\left\{ \begin{array}{l} m = 4 \\ m = 8 \end{array} \right.$	$\left\{ \begin{array}{l} 1\ N/100 \text{ iodine} \\ 1\ N/1000 \text{ ..} \end{array} \right.$	10 days.	
		$\left\{ \begin{array}{l} 1\ N/100 \text{ ..} \\ 1\ N/1000 \text{ ..} \end{array} \right.$	5 hours.	
		$\left\{ \begin{array}{l} 1\ N/100 \text{ ..} \\ 1\ N/1000 \text{ ..} \end{array} \right.$	8 days.	
		$\left\{ \begin{array}{l} 1\ N/100 \text{ ..} \\ 1\ N/1000 \text{ ..} \end{array} \right.$	30 mins.	
Carbon (c)	$\left\{ \begin{array}{l} m = 4 \\ m = 8 \end{array} \right.$	$\left\{ \begin{array}{l} 1\ N/100 \text{ ..} \\ 1\ N/1000 \text{ ..} \end{array} \right.$	135 mins.	
		$\left\{ \begin{array}{l} 1\ N/100 \text{ ..} \\ 1\ N/1000 \text{ ..} \end{array} \right.$	30 secs.	
Carbon (d)	$\left\{ \begin{array}{l} m = 4 \\ m = 8 \end{array} \right.$	$\left\{ \begin{array}{l} 1\ N/100 \text{ ..} \\ 1\ N/1000 \text{ ..} \end{array} \right.$	9 hours.	
		$\left\{ \begin{array}{l} 1\ N/100 \text{ ..} \\ 1\ N/1000 \text{ ..} \end{array} \right.$	30 secs.	

In the case of carbon (a), there appears to be no possibility of complete bleaching within a reasonable period.

In all the preceding experiments where complete bleaching was obtained, the carbon containing the iodine was transferred to a small stoppered flask and pure chloroform added, and in no case was any iodine extracted by the chloroform even after a period of twenty-four hours.

The relative activities of the four specimens of carbon used in the previous series were determined by treating 1 gram of the carbon with 25 c.c. of *N*/10-iodine solution for twenty-four hours:

(a) Original carbon as received, heated at 100°.	(b) Carbon heated in a vacuum for 2 hours at 600°.
$x/m = 0.1016$; $a - x = 0.8636$.	$x/m = 0.2616$; $a - x = 0.2336$.
(c) Carbon heated in a vacuum for 2 hours at 900°.	(d) Recovered carbon from series (b).
$x/m = 0.2817$; $a - x = 0.1432$.	$x/m = 0.2789$; $a - x = 0.1544$.

Second Series.—In this series of experiments the carbon was treated with iodine solutions for a definite period, during which it sorbed iodine from solution. The solution was then filtered off and the carbon rapidly transferred to a stoppered flask. The amount of iodine left in solution was estimated, and from this value the quantity of iodine in the carbon was calculated. The carbon containing the iodine was treated with pure solvent in the proportion of 15 c.c. of solvent to 1 gram of carbon, and the iodine in the solution again estimated after a definite period. The carbon was again treated with pure solvent and the iodine in the solution again estimated. These operations were repeated until no further iodine passed from the carbon to the chloroform.

The solutions were filtered through a thin pad of specially prepared asbestos, and a number of blank experiments showed that no appreciable quantity of iodine was retained by the asbestos under the conditions of the experiment. The treatment with pure solvent was generally for twenty-four hours; treatment for longer periods did not materially increase the amount of iodine extracted, hence equilibrium had been established within twenty-four hours.

Results.—

In experiments 1—4, the carbon used had been prepared as in (b) of the first series, and that used in experiment 5 prepared as in (d) of the first series.

Treatment of carbon.	x/m before treatment with pure solvent.	x/m when no detectable iodine is removed by solvent.	Total number of treatments with pure solvent.
1. <i>N</i> /10-Iodine solution for 24 hours. $m = 4$.	0.2614	0.2552	8
2. <i>N</i> /100-Iodine solution for 6 days. $m = 4$.	0.0308	0.02966	6
3. <i>N</i> /100-Iodine solution for 7 days. $m = 8$.	0.0158	0.01517	2
4. <i>N</i> /50-Iodine solution for 4 hours. $m = 4$.	0.0597	0.0588	2
5. <i>N</i> /10-Iodine solution for 24 hours. $m = 4$.	0.2816	0.2691	8

The above results indicate that the amount of iodine which can be retained by the carbon in contact with pure solvent is determined by the conditions under which the iodine was originally sorbed. For example, in experiment 1 the carbon retained 25 per cent. of its weight of iodine in contact with pure solvent, whereas in experiment 2, although the original iodine content was only 3 per cent., iodine was given up on treatment with pure solvent. The main difference between the two experiments was simply the concentration of the solution from which the iodine was originally sorbed. These results cannot be adequately explained on the assumption that iodine alone is sorbed; the liquid solvent also is sorbed. The amount of liquid solvent sorbed is probably very small in the more concentrated solutions, but relatively great in weak solutions.

Summary.

1. Four grams of a highly active sugar carbon will bleach 100 c.c. of *N*/100-iodine solution in a few minutes, whilst *N*/1000-iodine solution is bleached immediately. The bleaching in these cases is the result of adsorption.

2. A moderately active carbon requires several days for complete bleaching, which is therefore the combined result of both adsorption and absorption.

3. The amount of iodine which can be retained by the carbon in contact with pure solvent varies with the concentration of the solution from which the iodine was originally sorbed, and appears to be approximately proportional to it.

4. Carbon recovered from previous experiments showed marked increase in activity when freed from iodine.

5. Both solvent and solute are sorbed by the carbon, the relative proportions being mainly determined by the concentration of the iodine solution.

CXLI.—*Change of Properties of Substances on Drying.*
Part II.

By HERBERT BRERETON BAKER.

A YEAR ago, an account was given of the change of properties exhibited by many substances after drying by phosphoric oxide for nine or ten years (T., 1922, **121**, 568). In most of the experiments described below, I had the advantage of the co-operation of Prof. A. Smits of Amsterdam, who spent a fortnight in my laboratory in December last, repeating former determinations and aiding me in making new ones.

Boiling Point.—A puzzling feature of the experiments described last year was that whilst a thermometer immersed in the dried liquid indicated a boiling point of 14 to 62 degrees higher than the normal, a thermometer hanging in the vapour showed at most one or two degrees rise above the normal boiling point. This discrepancy can now be explained. In the earlier experiments, the determination was stopped as soon as an apparently steady condition had been attained. This was done in order to conserve these practically irreplaceable liquids, in order to see if any further change takes place with further drying. At Prof. Smits's instigation, I resolved to sacrifice one of the small flasks of dried benzene, in order to try to elucidate the difficulty. The flask had been set drying in 1913 by Mr. C. E. Sladden.

The neck of the flask was closed by a paraffined cork, through which the thermometer passed, instead of being drawn out and sealed as in the other experiments. There were about 15 c.c. of the dried liquid in the flask. The tip of the delivery tube was broken under dried mercury, and the temperature of the oil-bath slowly raised to 105° without any ebullition taking place. The thermometer in the vapour, when evaporation through the mercury was readily apparent, indicated a temperature of 81° (1° only above the normal boiling point), but as the evaporation proceeded the temperature rose to 87°, just before the last portion of the liquid had disappeared. This seems to indicate that a true fractional distillation was taking place, the non-associated liquid coming off in the earlier stages.

Melting Points.—The melting point of dried sulphur given in my former paper was 117.5°. Prof. Smits redetermined this, and found a melting point range of 116.8°–118.5°.

The melting point of bromine, dried since 1913 (boiling point 118°), was found to be –4.5°; that of bromine purified in the same way and dried by only a few days' contact with phosphoric oxide was found to be –7.3° (boiling point 59°).

Sulphur Trioxide.—There was in the laboratory a tube, shown at the meeting of the British Association in 1894, containing dried sulphur trioxide and copper oxide, which were found not to react when moisture was removed. The part of the tube containing phosphoric oxide had been sealed off, probably in 1912. It is unlikely that the inert copper oxide could have influenced the melting point of the sulphur trioxide, which was found to be 61.5° . A determination with sulphur trioxide which had been drying for a short time only gave a melting point of 50° . The dried sulphur trioxide changed on melting into the β -modification, the melting point of which was found to be 15.5° , compared with 14° . In an attempt to get back to the α -modification rapidly, the tube was immersed in liquid air, but a crack developed at the seal, so that further determinations could not be made.

Benzene.—The melting point of liquid dried for ten years was found to be 6.0° . The melting point of the same benzene which had been dried for a month only by phosphoric oxide and then distilled was found to be 5.4° .

Vapour Densities.—It has been possible to make only two determinations as yet of the vapour density of the long-dried liquids, by reason of the fact that the liquids must be sealed off in bulbs without contact with air, and it chanced that the apparatus in two cases only was provided with bulbs on the delivery tubes. These were ether which had been dried since 1913 and had a boiling point of 83° , and methyl alcohol, dried for the same length of time, which had a boiling point of 120° . The apparatus used was the modified Victor Meyer apparatus described in a former paper (T., 1900, 77, 647). The vapour density of the ether was 81.7, instead of the normal 37. Methyl alcohol, dried since 1913, gave a vapour density of 45, instead of the normal 16, the molecular weight indicated being nearly three times the normal figure.

Summary.

1. A definite fractional distillation of dried benzene has been effected, the highest temperature of the vapour observed being 87° .
2. The melting points of sulphur trioxide (dried for twenty years), bromine (dried for ten years), and benzene (dried for ten years), have been found to be 61° , 4.5° , and 6° , respectively.
3. The vapour density of ether (dried for ten years) has been found to be 81.7, more than double the normal, and of methyl alcohol, dried for the same length of time, to be 45, compared with the normal 15.

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[Received, May 3rd, 1923.]

CXLI.—*The Molecular Refractions of Chloro-,
Dichloro-, and Chlorobromo-acetates.*

By PAULE LAURE VANDERSTICHELE.

THE molecular refractions of a number of chlorine and bromine compounds have been determined by different investigators. The atomic refractivities of chlorine and bromine in these substances are only approximately constant, the variations observed betraying the effect, on the refractive power of the halogen atom, of the molecular structure in which it occurs. The determination of the molecular refractions of a systematised group of chlorine and bromine compounds is described below, and an attempt is made to trace possible constitutive influences in connexion with the halogen values. The use of $\alpha\beta$ -dichlorovinyl ethyl ether for the production of chloro-, dichloro-, chlorobromo-acetates and the corresponding acid chlorides (Crompton and Vanderstichele, T., 1920, **117**, 691; Crompton and Triffitt, T., 1921, **119**, 1874) provided suitable material for this investigation.

The substances dealt with were acetic, monochloro-, dichloro-, and chlorobromo-acetic acids, their chlorides, and their ethyl, phenyl, and *p*-tolyl esters. The molecular refractions of fifteen of these compounds were specially determined for the purpose. Eisenlohr's values are used for acetic acid and ethyl acetate, and Brühl's values for acetyl chloride, ethyl monochloroacetate, and ethyl dichloroacetate. The results obtained should:

1. indicate the variations of the refractivities of chlorine and bromine, in compounds of analogous structure.
2. illustrate the effect, on the molecular refraction, of the introduction of a second halogen atom in a molecule, when attached to the carbon to which the first halogen atom belongs.

EXPERIMENTAL.

Determination of the Density.—The densities were determined with a Ramsay pycnometer. The quantities of pure material available were usually small, and the pycnometers used had a capacity of about 3 c.c. All the densities are referred to that of water at 4°.

Determination of the Refractive Index.—The refractive indices were determined by means of a Pulfrich refractometer. As the latter was fitted with a heating apparatus, readings could be taken

at different temperatures. In the case of substances which are solid at the ordinary temperature, the determinations were carried out for temperatures just above the melting point. Sodium light was employed in every case.

Calculation of the Molecular Refraction.—The molecular refraction was calculated according to the Lorentz-Lorenz formula. The refractive indices having been determined for different temperatures over a range of about 6° , the corresponding values of the refractive index and the temperature were represented graphically. Falk (*J. Amer. Chem. Soc.*, 1909, **31**, 806) has shown that, over small ranges of temperature, the refractive index is a linear function of the temperature. The results obtained were in agreement with Falk's statement, and the value used for the calculation of the molecular refraction was found by interpolation for a suitable temperature.

The densities were usually determined for at least three different temperatures and the density for the required temperature was obtained from the curve connecting these values.

As several of the substances examined were available in small quantities only, and some of them are, moreover, fairly hygroscopic, their purification was somewhat troublesome. But, except in the case of chlorobromoacetyl chloride, the values quoted for the molecular refractions are probably trustworthy to the first place of decimals.

The molecular refraction calculated on the Lorentz-Lorenz expression increases, according to Eykman, by about 0.003 for a rise of temperature of 1° . In order to reduce the results obtained to the same temperature, an appreciable correction of the values for relatively high-melting solids would be necessary. This correction would not, however, exceed -0.147 , the amount involved in the case of monochloroacetic acid, and in most other cases would be considerably smaller.

Methods of Preparation.—Monochloroacetic acid, dichloroacetic acid, and phenyl acetate were purified from the commercial products; *p*-tolyl acetate was obtained by the action of acetyl chloride on *p*-cresol. The remaining compounds were prepared from $\alpha\beta$ -dichlorovinyl ethyl ether (*loc. cit.*).

The purity of the specimen used was indicated by the constancy of its melting or boiling point. Chlorobromoacetyl chloride, the preparation of which is given below, was the only substance which could not be obtained in a trustworthy condition.

Preparation of Chlorobromoacetyl Chloride.—The requisite quantity of bromine was added to $\alpha\beta$ -dichlorovinyl ethyl ether (Crompton and Trifitt, *loc. cit.*) and the liquid allowed to stand out of contact

with the air for several weeks. It was then submitted to fractional distillation. Ethyl bromide was collected below 50°. The rest of the mixture came over mainly between 132° and 165°, but no distinct boiling point was observed. After several fractionations, two distillates were isolated, the one boiling from 132° to 135° (uncorrected), the other from 135° to 139° (uncorrected), which consisted very largely of chlorobromoacetyl chloride. The values obtained for the density and the refractive index of these two fractions were unsatisfactory and betrayed an appreciable difference of composition.

Fraction 132—135°.

$$t^{\circ} = 19^{\circ}; d_4^{20} = 1.9402; n_D^{20} = 1.5030; \text{whence } [R_L]_D, 29.232.$$

Fraction 135—139°.

$$t^{\circ} = 18^{\circ}; d_4^{20} = 1.9665; n_D^{20} = 1.5060; \text{whence } [R_L]_D, 28.989.$$

The fraction obtained for the range of temperatures 132—135° was distinctly the larger of the two, but it may have contained traces of α,β -dichlorovinyl ethyl ether (b. p. 128°). The fraction 135—139° may be mixed with a little chlorobromoacetyl bromide, as the value quoted for its molecular refraction seems to indicate the presence of some impurity of higher molecular weight. Further purification of the small quantities of final product obtained was impossible, owing to the difficulty of handling this material.

Preparation of Chlorobromoacetic Acid.—Chlorobromoacetyl chloride was converted into chlorobromoacetic acid by addition of water. The crude product obtained was purified by fractional distillation. The main bulk of the liquid distilled from 207° to 212° (uncorrected) and solidified on cooling.

Chlorobromoacetic acid, which has not previously been obtained in the solid state (Cech and Steiner, *Ber.*, 1875, 8, 1174; Conrad and Brückner, *Ber.*, 1891, 24, 2996), forms colourless crystals. The melting point determined in the usual manner is 25°, but the solidifying point when the thermometer is immersed in the liquid is 23.8°. It boils with some decomposition at 210—212° (uncorr.), 767 mm.

The data obtained are given in the table below, in which t is the temperature at which the density d_t and the refractive index n_D were determined, and $[R_L]_D$, the molecular refraction calculated from d_4^t and n_D^t .

	<i>t.</i>	d_4^{20}	n_D^{20}	$[R_L]_D^{20}$
Monochloroacetic acid	65°	1.3703	1.4297	17.800
Dichloroacetic acid	19	1.5691	1.4667	22.783
Chlorobromoacetic acid	30.6	1.9848	1.5014	25.763
Monochloroacetyl chloride	20	1.4177	1.4535	21.550
Dichloroacetyl chloride	16	1.5315	1.4638	26.539
Ethyl chlorobromoacetate	24	1.5857	1.4659	35.182
Phenyl acetate	20	1.0777	1.5088	37.684
Phenyl monochloroacetate	44	1.2202	1.5140	42.111
Phenyl dichloroacetate	52	1.2967	1.5103	47.296
Phenyl chlorobromoacetate	52	1.5289	1.5322	50.574
<i>p</i> -Tolyl acetate	17	1.0512	1.5026	42.178
<i>p</i> -Tolyl monochloroacetate	35	1.1840	1.5150	46.994
<i>p</i> -Tolyl dichloroacetate	64	1.2381	1.5027	52.251
<i>p</i> -Tolyl chlorobromoacetate	62	1.4626	1.5242	55.138

The values for the molecular refractions, including those of acetic acid, acetyl chloride, ethyl acetate, ethyl monochloroacetate, and ethyl dichloroacetate, are arranged in the following table for purposes of comparison. No attempt was made to reduce these values to a standard temperature, as the correction to be applied is some, what indeterminate and would not in any case essentially affect the conclusions given below.

	Acetyl.	Δ .	Chloro-acetyl.	Δ .	Dichloro-acetyl.	Δ .	Chloro-bromo-acetyl.
Calculated average differences:							
Brühl and Conrady	4.947		4.917		2.920		
Eisenlohr	4.867		4.867		2.898		
Acid	13.95	4.750	17.800	4.983	22.783	2.978	25.761
Chloride	16.85	4.700	21.550	4.989	26.539	2.693	29.22
Ethyl ester	22.38	4.530	26.91	5.270	32.18	3.002	35.182
Phenyl ester	37.684	4.427	42.111	5.185	47.296	3.278	50.574
<i>p</i> -Tolyl ester	42.178	4.816	46.994	5.257	52.251	2.887	55.138

Conclusions.

Attention may be directed to the following points:

1. The molecular refractions obtained for monochloro-, dichloro-, and chlorobromo-acetyl chloride confirm the high value attributed by Le Blanc (*Z. physikal. Chem.*, 1889, **4**, 554), Brühl (*ibid.*, 1891, **7**, 178), and Eisenlohr (*ibid.*, 1910, **75**, 585) to the refractivity of the chlorine atom when combined with a carbonyl group.

2. If we consider the increase in the molecular refraction corresponding to the introduction of one atom of chlorine in the acetyl group (columns 2, 3, and 4 in the above table; mean value of $\Delta 4.645$), we find that the (Cl) - (H) differences diverge from the mean value by not more than 4.7 per cent.

3. If we consider the effect of the introduction of a second atom of halogen in the chloroacetyl group, on the molecular refraction of the compound (columns 4—8: for chloroacetyl \rightarrow dichloroacetyl

and for chloroacetyl \rightarrow chlorobromoacetyl the mean values of Δ are 5.137 and 8.210 respectively), we find that the (Cl)—(H) differences diverge from the mean value by not more than 3.0 per cent. and the (Br)—(H) differences by not more than 3.1 per cent. (omitting the doubtful value for chlorobromoacetyl chloride).

4. If we compare the three above sets of increments with the values for (Cl)—(H) and (Br)—(H) deduced from the average atomic refractivities calculated by Conrady and Eisenlohr,

	(Cl)—(H).	(Br)—(H).
Brühl-Conrady's average value ...	4.947	7.876
Eisenlohr's average value	4.867	7.765
Mean increment observed	4.645	8.210
	Effect produced by the introduction of <i>one</i> atom of chlorine in the acetyl group.	Effect produced by the introduction of a <i>second</i> atom of chlorine in the acetyl group.
		Effect produced by the introduction of an atom of bromine in the chloroacetyl group.

we find that the mean increase in refraction caused by the first atom of chlorine is distinctly smaller, and the mean increase in refraction caused by the second atom of halogen distinctly larger, than the values for (Cl)—(H) and (Br)—(H) deduced from the Brühl-Conrady and Eisenlohr averages.

As far as this group of substances is concerned, the introduction of a second atom of halogen in the chloromethyl group causes a measurable exaltation of the molecular refraction.

I wish to express my thanks to Mr. H. Crompton, who suggested the subject of this work, and to whom I am indebted for much direction and advice.

BEDFORD COLLEGE.

[Received, February 10th, 1923.]

CXLIII.—*The Velocity of Reaction in Mixed Solvents.*
Part V. a. The Velocity of Formation of Quaternary Ammonium Salts. b. The Study of an Intramolecular Change.

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 SCARBOROUGH.

IN former communications (T., 1921, **119**, 970 *et seq.*), the velocity of saponification of certain ethyl esters of monocarboxylic acids by a number of bases and at three temperatures has been recorded.

A consideration of the results and of the curves showing the relation between the velocity coefficient, k , and the percentage composition by weight of the ethyl alcohol-water mixtures seems to show that the form of the curve is dependent on the power of the two solvents to form complexes. Further, it was found that that section of the curve between any two discontinuities approached very closely to a straight line; and finally it appeared probable that a discontinuity in the curve became more or less pronounced as the power of the solvent complex to form a further complex with one of the reactants increased or decreased.

A series of deductions drawn from a study of a single type of reaction, even if this reaction is studied with a full consideration of each possible variant, forms an inadequate basis on which to build a working hypothesis.

It seemed desirable to extend the investigation in three ways:

(a) To select a reaction which is bimolecular, but which proceeds more rapidly in water than in alcohol, and is chemically different from the type of reaction already studied.

These requirements seem to be satisfied in the addition of pyridine to bromoacetic ester; a reaction formerly studied by Clarke (T., 1910, 97, 416).

(b) To select a bimolecular reaction similar in type to that chosen to meet the requirements of (a) and to change the solvents in such a way that the probability of complex formation* is appreciably reduced.

The reaction between trimethylamine and *p*-nitrobenzyl chloride in benzene-nitrobenzene mixtures as solvent seemed suitable. This reaction has been studied by von Halban (Z. physikal. Chem., 1913, 84, 129).

(c) To select a monomolecular reaction proceeding more rapidly in water than in alcohol. This object was not attained, but a reaction studied by Dinuroth (Annalen, 1904, 335, 1), the tautomeric change of methyl 5-hydroxy-1-phenyl-1:2:3-triazole-4-carboxylate into methyl 1-phenyl-5-triazolone-4-carboxylate, which proceeds faster in alcoholic solution than in aqueous solution, seemed a suitable substitute.

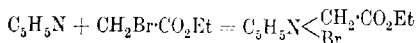
(a) *The Formation of Quaternary Ammonium Compounds in Binary Solvent Media.*

The rate of formation of quaternary ammonium compounds has been studied by numerous investigators and whilst the nature of the base and of the halogenated substance has been varied within very wide limits, and the solvent changed between such extremes as *n*-hexane and nitromethane, in few cases has a single pair of

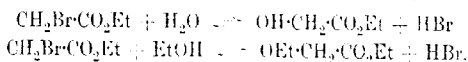
solvents been examined in more than one or two mixtures and at the most five.

Hemptinne (*Z. physikal. Chem.*, 1899, 28, 225) made a study of the addition of ethyl bromide and ethyl iodide to trimethylamine in binary and ternary solvent media, but for any pair or trio of solvents the number of mixtures examined was limited to five. In this work, the relation between the value of k and the percentage composition of the solvent is assumed to be linear throughout and the percentage deviation is ascertained between the experimentally determined and the calculated values of a 50 per cent. mixture. The deviation found with a pair of solvents of the same chemical class is within the experimental error, but for a binary mixture composed of solvents of very different classes the deviation amounted to an average of more than 60 per cent.

The first reaction to be studied was the addition of bromoacetic ester to pyridine in alcohol-water mixtures at 45°. The addition proceeds according to the equation



and is stated to be bimolecular and irreversible. It was found, however, that the reaction is not strictly bimolecular, as the value of k tends to increase slightly with the time and towards the completion of the reaction rises very rapidly. The reaction probably consists in two simultaneous reactions, (a) the formation of the quaternary ammonium compound according to the equation given above, a reaction which, comparatively, proceeds at a high speed, and (b) the interaction between the bromoacetic ester and the alcohol and the water of the solvent medium according to the equations

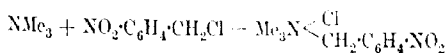


reactions which are comparatively slow and the effect of which is scarcely appreciable until some 50 per cent. of the reaction is completed.

The results are shown in Tables I and II and in Fig. 1.

The second example of the formation of a quaternary ammonium salt was the addition of *p*-nitrobenzyl chloride to trimethylamine in solvent mixtures of benzene and nitrobenzene at 30°.

The addition proceeds according to the equation

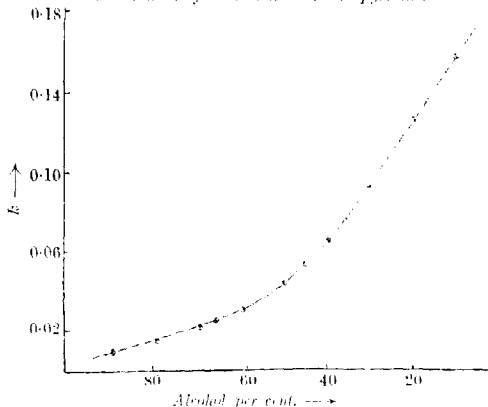


This reaction appears to be strictly bimolecular and proceeds to completion. The quaternary ammonium salt is comparatively

insoluble in the benzene-nitrobenzene mixtures, and if large concentrations of the amine and of the chloride are used, the ammonium salt is precipitated and the constant tends to become very irregular; usually the constant is steady for a period, then follows a rapid fall and finally the constant tends to become steady once more. An attempt was made to use the concentrations of the reactants employed by von Halban (*loc. cit.*), and this irregular behaviour of the constant was very noticeable if the reaction was allowed to proceed to about 90 per cent. of completion; consequently the concentrations were maintained at a smaller value and all irregularities disappeared. As the values of k in the single solvents were very

FIG. 1.

The addition of bromoacetic ester to pyridine.



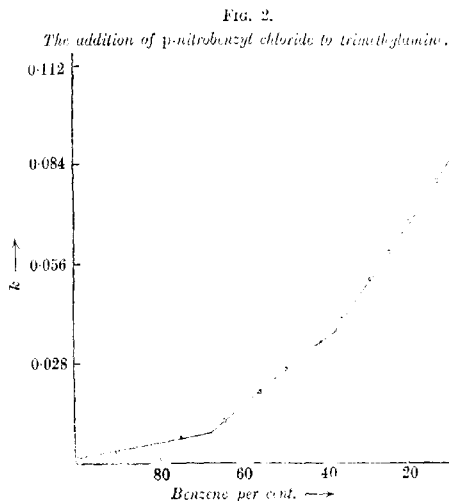
low in comparison with those obtained by von Halban, the effect of the initial concentrations of the reactants was examined over a wide range, the upper limit being fixed so that the reaction mixture was homogeneous up to an 80 per cent. conversion. Under these conditions, the reaction was found to be strictly bimolecular and independent of the initial concentrations.

The experimental results are shown in Tables IV and V and in Fig. 2.

A consideration of the results obtained for the velocity of addition of bromoacetic ester to pyridine in alcohol-water mixtures shows that we are dealing apparently with a reaction which is independent of the possible formation of alcohol water complexes. The curve shows that as the percentage of water in the solvent medium is

increased the value of k rises smoothly and slowly until about 40 per cent. of water is present; after which the value of k rises sharply with the increase of the water content of the solvent. It is very noticeable that the marked discontinuities and sudden changes of direction in the curve observed in the case of the saponification of an ester by a strong base are absent, and the curve, by comparison, appears smooth and continuous.

Attempts have been made to divide the curve into a series of linear sections; the results are, however, unsatisfactory, since each section can be made to include a variable number of points without



the difference between the observed and the calculated values of k being outside the experimental error. The relation between k and the composition of the solvent medium could not be expressed as a hyperbolic or logarithmic function.

The physical properties of alcohol-water mixtures and the rate at which an ester is saponified by a strong base in alcohol-water mixtures have been considered to show the presence of alcohol-water complexes at 45°. Further, it will be shown that the rate of addition of *p*-nitrobenzyl chloride to trimethylamine in benzene-nitrobenzene mixtures seems to indicate the presence of solvent complexes.

The continuous curve obtained for the addition of bromoacetic

ester to pyridine would seem impossible of explanation on the assumption that the solvents do not form complexes or that the type of chemical reaction studied is unsuitable.

The study of the influence of the base on the velocity of saponification of an ester showed that the base could play a so far decisive rôle that certain complexes were apparent only with certain bases.

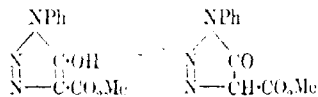
A consideration of the above facts would seem to indicate that a discontinuous curve is to be ascribed to a joint effect of base and solvent complex. The most feasible explanation of this joint action appears, to the authors, to be a union between the solvent complex and one of the reactants. Thus the continuous curve for the reaction between pyridine and bromoacetic ester would be explained on the assumption that there is no union between one of the reactants and the solvent complex.

The consideration of the results and curve obtained in the reaction between *p*-nitrobenzyl chloride and trimethylamine indicates that the only possible division of the curve is into three linear sections. This result was unexpected, and every means of confirming it have been taken; each confirmatory measurement has only served to verify the initial conclusions. The points of intersection of the sections occur at 29 and 59.4 per cent. of nitrobenzene and correspond to the complexes $4C_6H_6 \cdot C_6H_5 \cdot NO_2$ and $C_6H_6 \cdot C_6H_5 \cdot NO_2$, respectively; such complexes would actually require the compositions 28.4 and 61 per cent. of nitrobenzene, respectively.

The physical properties of benzene-nitrobenzene mixtures seem to have undergone but little examination, and the only physical constant which appears to have been recorded is the freezing-point curve. This curve shows no evidence of complex formation, and the only matter of interest is the fact that the eutectic point occurs at a composition of 48.7 molecules per cent., or 59.9 per cent. by weight of nitrobenzene.

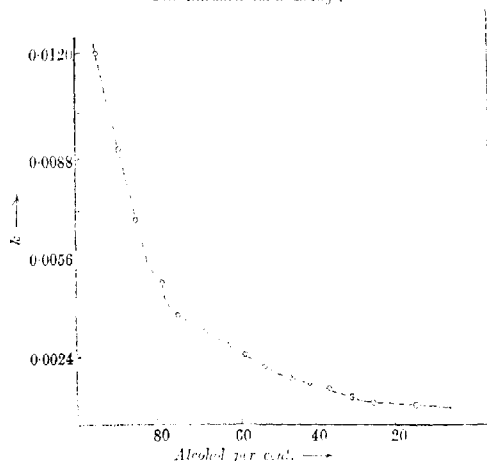
(b) *The Tautomeric Change of Methyl 5-Hydroxy-1-phenyl-1:2:3-triazole-1-carboxylate.*

This tautomeric change has been examined by Dimroth (*loc. cit.*) in a number of solvents with the object of verifying the theory that the velocity coefficient is a function of the solubility of the reactant or of the product in that particular solvent. The conversion was studied in alcohol-water mixtures at 30°. The reaction is represented by the equation



The reaction is monomolecular and reversible, although in alcohol the equilibrium position is represented by 300:1::keto:enol, and the corresponding ratio in water is 14:1. Thus the constant found had to be corrected for the reverse reaction. This correction was made by determining the equilibrium position for selected alcohol-water mixtures. This reaction is of special interest, as the value of k is greater in alcohol than in water, the reverse of what is found in the case of the saponification of an ester. The results are shown in Tables VI and VII and in Fig. 3.

FIG. 3.
The intramolecular change.



The curve again shows similarities to those obtained in the saponification of an ester. Thus there is a marked change in direction at 81.7, at 56.4, and at 31.4 per cent. of alcohol, compositions which seem to indicate the complexes $5C_2H_5\cdot OH, 3H_2O$, $C_2H_5\cdot OH, 2H_2O$, and $C_2H_5\cdot OH, 6H_2O$. The complexes represented by the compositions 81.2 and 31.4 per cent. of alcohol seem to be well established. The complex $C_2H_5\cdot OH, 2H_2O$ has not been observed before; data previously obtained indicated a complex $3C_2H_5\cdot OH, 5H_2O$, which has the composition 60.5 per cent. of alcohol. It has been shown, however, that the complex $C_2H_5\cdot OH, 2H_2O$ has been deduced from most other physical measurements.

EXPERIMENTAL.

1. *The Addition of Bromoacetic Ester to Pyridine in Ethyl Alcohol-Water Mixtures at 45°.*

The bromoacetic ester was prepared from acetic acid by the usual method and purified by repeated fractional distillations; the fraction boiling at 159° was retained and distilled under reduced pressure. The pyridine (Kahlbaum) was distilled and the fraction boiling at 116° retained. The ethyl alcohol-water mixtures were prepared in the manner previously described.

The progress of the reaction was followed by titration with silver nitrate and ammonium thiocyanate—Volhard's method—using iron alum as an indicator. The silver nitrate was made up in bulk and stored in blackened reservoirs; the ammonium thiocyanate was also made up in bulk and of approximately the same strength.

The reaction mixture was made up by weighing out each of the reactants and making up to a given volume; equimolecular quantities of the reactants were mixed in the cold; 10 c.c. of this solution were transferred to a small conical flask immersed in the thermostat, and the flask was securely closed. The zero time was taken as that moment at which 5 c.c. of the mixture had been transferred to the conical flask. After the lapse of a given time, a flask was withdrawn, an excess of standard silver nitrate solution run in from a burette, a small quantity of nitric acid added, and the excess of silver nitrate titrated with the standard ammonium thiocyanate solution. The results are shown in Table I; the value of k is the mean of eight determinations. The velocity coefficient is calculated from the formula

$$k = x/at \cdot (a - x),$$

where a is the concentration of the reactants in gram-mols. per litre, and t is the time in minutes.

TABLE I.

Alcohol per cent.	C_{reactant}	Limit k .	k .
90	0.250	0.0123—0.0116	0.0119
80	0.250	0.0175—0.0165	0.0172
70	0.250	0.0237—0.0232	0.0233
66.32	0.1667	0.0262—0.0258	0.0260
60	"	0.0323—0.0315	0.0319
50	0.125	0.0455—0.0450	0.0452
45	"	0.056—0.053	0.0545
40	"	0.065—0.0635	0.0645
35	"	0.081—0.077	0.078
30	0.0833	0.098—0.095	0.096
20	0.0555	0.134—0.120	0.127
10	0.0667	0.164—0.157	0.162

In Table II are shown representative results for two alcohol-water mixtures, indicating the limits between which k varied and the extent to which the reaction was examined.

TABLE II.

66.32 Per cent. alcohol. $a = 0.1667$.			39 Per cent. alcohol. $a = 0.0833$.		
AgNO ₃ = 0.04730N; NH ₄ CNS = 0.04616N.					
t .	Change per cent.	k .	t .	Change per cent.	k .
55	19.13	0.0258	35	22.24	0.0980
68	22.70	0.0259	45	26.62	0.0967
83	26.59	0.0262	53	30.20	0.0979
100	30.23	0.0260	62	33.26	0.0964
114	33.04	0.0260	75	37.70	0.0967
130	36.00	0.0259	83	39.78	0.0955
145	38.60	0.0260	92	41.66	0.0950
210	47.62	0.0260	97	43.25	0.0953
230	49.70	0.0260	107	46.10	0.0959
Mean 0.0260			Mean 0.0962		

2. The Addition of *p*-Nitrobenzyl Chloride to Trimethylamine in Benzene-Nitrobenzene Mixtures.

The benzene was prepared from the commercial benzene by washing with sulphuric acid, freezing out the benzene three times and rejecting about one-third of the liquid at each operation, and finally distilling over sodium. The nitrobenzene was prepared from the purified benzene and fractionated under ordinary pressure and then under reduced pressure.

The density curve for benzene-nitrobenzene was made using a pycnometer of about 20 c.c. capacity; a small bulb was sealed into one arm of the pycnometer to allow for the expansion of the benzene, and small glass caps were ground on to each arm. All measurements were made at 15° and compared with the density of water at 4°.

The method employed to determine the composition of the mixture was to weigh out about 12 grams of nitrobenzene (benzene) into a weighing bottle with a carefully ground-in stopper; benzene (nitrobenzene) was run into the bottle from a burette, the volume being calculated to give a mixture of approximately the required composition, and the bottle reweighed. Three determinations of the density of the mixture were made. The curve was slightly concave and in order to obtain the density at intermediate points the assumption was made that the curve was a series of straight lines between successive points, when the maximum error involved is 5 in the fifth decimal figure.

The results are recorded in Table III.

TABLE III.

Per cent. benzene.	d_4^{15} .	Per cent. benzene.	d_4^{15} .	Per cent. benzene.	d_4^{15} .
100	0.88453	62.96	0.98327	31.00	1.08650
93.42	0.89933	58.55	0.99635	24.77	1.10880
89.82	0.90996	55.49	1.00565	18.03	1.13446
85.71	0.92315	49.92	1.02283	13.58	1.15163
78.96	0.93839	45.98	1.03541	8.95	1.17006
72.31	0.95661	40.38	1.05395	4.66	1.18855
67.67	0.96988	35.81	1.06941	0	1.20870

The benzene-nitrobenzene mixtures were made up and their composition determined from the density data.

The trimethylamine was obtained as the hydrochloride (Kahlbaum), and the *p*-nitrobenzyl chloride was prepared from benzyl chloride by nitration according to the method described by Beilstein (*Annalen*, 1866, **139**, 337) and crystallised from ligroin until a constant m. p. 71° was obtained.

The method of preparing solutions for the measurements was to liberate the trimethylamine from the hydrochloride by warming with caustic potash solution, pass the gas through a series of tubes packed with soda-lime, and absorb it in the solvent, which was cooled in ice. The concentration of the base was determined by titrating two portions of this solution against 0.05N-hydrochloric acid, using as indicator a mixture of methyl-orange and sodium indigotin-sulphonate, prepared according to the method of Luther (*Chem. Ztg.*, 1907, **31**, 1172).

The *p*-nitrobenzyl chloride solution was made by direct weighing.

The reaction velocity was determined at $30^\circ \pm 0.05^\circ$ in the following manner. A number of small reagent bottles, carefully stoppered with rubber stoppers, were immersed in the thermostat; a bottle was withdrawn, and 5 c.c. of each of the reactant solutions were run in from a pipette, and the bottle was replaced in the thermostat. Zero time was taken as that point at which the two solutions were mixed. After a given interval, a bottle was withdrawn, excess of standard silver nitrate solution was added, followed by a few c.c. of nitric acid and ether, and the mixture was vigorously shaken in order to coagulate the silver chloride (*Z. anorg. Chem.*, 1909, **63**, 330). The excess of silver nitrate was titrated against ammonium thiocyanate, using iron alum as indicator. The results are shown in Table IV. The velocity coefficient is calculated from:

$$k = 2.302/(a - b)t \cdot \log_1(a - x) \cdot b/(b - x) \cdot a',$$

where a and b are the initial concentrations of the reactants in gram-mols. per litre and t is the time in minutes.

TABLE IV.

Benzene per cent.	Catalase	Chloride	Limit k .	k .
100	0.0904	0.0876	0.00164—0.00153	0.00158
91.27	0.1379	0.1145	0.00412—0.00393	0.00404
83.43	0.1187	0.0851	0.0072—0.00695	0.00703
74.30	0.1327	0.0769	0.0109—0.0105	0.0106
63.58	0.0623	0.1084	0.0177—0.0163	0.0169
56.40	0.0617	0.0755	0.0227—0.0218	0.0221
49.58	0.1224	0.1427	0.0275—0.0262	0.0266
42.57	0.1288	0.0999	0.0332—0.0320	0.0323
36.86	0.1126	0.0576	0.0399—0.0378	0.0387
30.41	0.2094	0.0674	0.0507—0.0488	0.0497
25.09	0.0611	0.0655	0.0579—0.0564	0.0571
20.26	0.0551	0.0825	0.068—0.0661	0.065
12.48	0.0465	0.0684	0.077—0.073	0.075
6.72	0.0734	0.0459	0.088—0.084	0.086
0	0.0460	0.0601	0.112—0.104	0.107

In Table V are shown two representative results for two benzene-nitrobenzene mixtures, indicating the limits between which k varied and the extent to which the reaction was examined.

TABLE V.

Benzene. Catalase 0.0904; Chloride 0.0876.			29.36 Per cent. benzene. Catalase 0.0551; Chloride 0.0825.		
t .	x .	k .	t .	x .	k .
1451	0.0149	0.00153	88	0.0184	0.064
1922	0.0195	0.00163	128	0.0237	0.064
2549	0.0238	0.00161	166	0.0288	0.068
3020	0.0268	0.00161	218	0.0333	0.064
3305	0.0283	0.00154	248	0.0351	0.067
3813	0.0322	0.00164	290	0.0373	0.066
4353	0.0336	0.00155	324	0.0388	0.065
4895	0.0353	0.00154	365	0.0400	0.063
Mean 0.00158			Mean 0.065		

A consideration of the results and of the curve shows that as the percentage of benzene in the solvent mixture is increased the value of k falls sharply until about 10 per cent. has been added; from this point the curve appears to consist of three linear sections. Assuming that these sections are perfectly linear up to the point of intersection, these points would occur at 59.4 and 29.0 per cent. of nitrobenzene, whereas the complexes $C_6H_6 \cdot C_6H_5 \cdot NO_2$ and $4C_6H_6 \cdot C_6H_5 \cdot NO_2$ require 61 and 28.4 per cent. of nitrobenzene, respectively.

(c) *The Conversion of Methyl 5-Hydroxy-1-phenyl-1:2:3-triazole-4-carboxylate into Methyl 1-Phenyl-5-triazolom-4-carboxylate in Alcohol-Water Mixtures.*

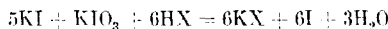
The methyl ester of the hydroxyphenyltriazole-carboxylic acid was prepared by Dimroth's method (*loc. cit.*) by the condensation of phenyl azide with malonic ester; it was stored as the stable hydrate

and dehydrated over phosphoric oxide in a desiccator just before use. The ketonic isomeride which was formed during the dehydration was removed by washing with pure dry ether.

The solvent mixtures were prepared as described in former communications. The reaction mixture was prepared by adding an appropriate amount of the enolic ester to the required alcohol-water mixture, shaking vigorously, filtering rapidly, and immersing in the thermostat for about five minutes.

The initial concentration was determined by taking 10 c.c. of the solution, adding to it a mixed solution of potassium iodide and iodate, and titrating the liberated iodine against standard sodium thiosulphate. The moment at which this sample was removed was considered as zero time. The potassium iodide solution contained 32 grams per litre and the potassium iodate solution 5 grams per litre; equal quantities of these solutions were mixed immediately before use.

The reaction is very simple to follow, as the enolic ester is strongly acidic, whereas the ketonic ester is neutral, and the former liberates iodine from the iodide-iodate solution according to the equation



(where HX is the enolic ester). Thus each molecule of the enolic ester liberates one atom of iodine. The reaction is monomolecular and the velocity coefficient is calculated from the equation

$$k = k_1 - k_2 = 1/t \cdot \log a/a - x,$$

where a is the initial concentration of the ester, t is the time in minutes, k_1 is the velocity of formation of the ketonic ester, and k_2 is the velocity of formation of the enolic ester.

The actual value of k_1 was determined by finding the equilibrium position in various alcohol-water mixtures and thus finding the relative value of k_2 . The results are shown in Table VI and in Fig. 3.

TABLE VI.

Alcohol per cent.	Limit k .	k_1 .	Alcohol per cent.	Limit k .	k_2 .
94.2	0.0119—0.0117	0.0119	*54.89	0.00140—0.00130	0.00140
*90	0.0089—0.0088	0.00895	*50	0.00120—0.00110	0.00121
85	0.0062—0.0061	0.00625	*45	0.00093—0.00091	0.000965
*80	0.00485—0.0047	0.00485	*40	0.00068—0.00062	0.00068
75	0.00375—0.00365	0.00375	*34.86	0.00048—0.00044	0.00048
70	0.0031—0.0029	0.00305	*30	0.00033—0.00030	0.00033
*65	0.00245—0.00230	0.00245	*19.34	0.000125—0.00011	0.00012
60	0.00195—0.00187	0.00195			

Values marked * have been determined in duplicate.

In Table VII are shown two representative results for two alcohol-water mixtures.

TABLE VII.

90 Per cent. alcohol.			19.34 Per cent. alcohol.		
<i>t.</i>	Titre.	<i>k.</i>	<i>t.</i>	Titre.	<i>k.</i>
0	17.25	—	0	10.15	—
49	11.20	0.0088	1211	8.80	0.000118
69	9.40	0.0088	1721	8.24	0.000122
89	7.80	0.0089	2959	7.00	0.000120
109	6.51	0.00895	4154	6.15	0.000120
129	5.50	0.00885	5548	5.35	0.000116
150	4.60	0.0088	5949	5.14	0.000115
	Mean	0.00885		Mean	0.000118

A consideration of the results and of the curve shows that the value of k_1 appears to be directly proportional to the composition of the solvent mixtures in the three linear sections into which the curve is divisible.

A fourth section is indicated by two points only, owing to the insolubility of the ester in solvent mixtures containing more than 80 per cent. of water.

The points of intersection occur at 81.7, 56.4, and at about 32 per cent. of alcohol. These results are in remarkable agreement with those obtained from a study of the saponification of esters in the same pair of solvents.

Summary.

(1) Two reactions have been examined in a solvent consisting of alcohol and water, and one in mixtures of benzene and nitrobenzene.

(2) The curves showing the relation between the value of k and the composition of the solvent show certain similarities: the curves appear to be built up of a number of straight lines which do not intersect at a point but pass from one section to the next by a slight curvature.

(3) The calculated points of intersection occur at such compositions of the solvent medium that complexes seem to be indicated.

(4) The points of discontinuity become more or less pronounced according to the nature of the reaction, and the differences in behaviour observed in the various reactions seem to indicate that a solvent complex only becomes marked when one of the reactants is capable of forming a further complex with the solvent complex.

(5) The complexes indicated in the reaction in alcohol-water mixtures are in close agreement with those previously found.

(6) Benzene and nitrobenzene seem to form at least two well-defined complexes.

The authors beg to express their thanks to the Government Grant Committee of the Royal Society for funds placed at their disposal which have defrayed the cost of the research.

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[Received, March 8th, 1923.]

CXLIV.—*Oxidation of Nickel Sulphide.*

By JOHN STANLEY DUNN and ERIC KEIGHTLEY RIDEAL.

THE mechanism of a number of heterogeneous reactions in which a solid catalyses the reaction between two gases or substances in solution has been examined in detail, but the case of a reaction between a solid and a dissolved substance under the influence of a soluble catalyst has not been extensively investigated.

It has been found that the oxidation of nickel sulphide suspended in water is a reaction of this type, and investigations have been made to determine the following factors:

- (1) The temperature coefficient of the reaction.
- (2) The influence of a soluble catalyst.
- (3) The connexion between catalytic action and adsorption of the catalyst on the surface of the nickel sulphide.

The literature available on the oxidation of metallic sulphides is meagre and in many cases untrustworthy. For instance, the atmospheric oxidation of some sulphides is attributed by one author to small quantities of ozone.

Pavia (*Mon. Sci.*, 1908, [iv], 22, 373) states that the reaction proceeds in two stages. Sulphur is first set free with the formation of the corresponding oxide. The sulphur is then oxidised to sulphuric acid and dissolves the oxide. He states, further, that these reactions are in general accelerated by sunlight.

Preparation of Sulphides.—When nickel monosulphide is prepared by precipitation from solution, it occurs in three polymorphic modifications, designated α , β , and γ , according to circumstances (Thiel, *Chem. Zentr.*, 1914, i, 18).

The α -sulphide is prepared as a spongy, black mass when freshly prepared ammonium sulphide is added to a solution of a nickel salt. It retains water very strongly and is comparatively active chemically. If, for instance, air is suddenly admitted to a vacuum desiccator in which α -nickel sulphide is drying, the temperature will rise rapidly to 50–60° owing presumably to rapid oxidation (see also de Clermont and Guizot, this Journal, 1877, 32, 190).

The β -sulphide is formed when hydrogen sulphide is passed through nickel acetate solution. It is a black precipitate, rather denser than the α -form, and is much more easily dried.

The γ -sulphide is produced when hydrogen sulphide is passed into nickel acetate solution, acidified with acetic acid. The resulting precipitate is boiled with 2*N*-hydrochloric acid, which converts some of the β -form to γ and dissolves the remainder. Thus pre-

pared, it is a grey powder with a pyritic lustre. It is much less active than either the α - or β -form.

The three forms of the sulphide were prepared as described above, washed by repeated decantation with distilled water, and finally with hot water on a Buchner filter. They were then dried by pressing between filter-paper, and the process was completed by standing in a vacuum over calcium chloride.

The β -form, which was examined in greatest detail, gives a suspension when dispersed in pure water which takes ten minutes or more to settle completely. The γ -form under similar conditions settles much more rapidly.

It was at first attempted to follow the course of the reaction by the estimation of the soluble nickel produced when carbon dioxide-free air was bubbled through a suspension of nickel sulphide. If this method be employed, water must be added to replace the sample withdrawn. This constitutes a serious drawback when a catalyst is present, however, for the original concentration of catalyst is undoubtedly changed by adsorption and the addition of catalyst solution at the original strength would be inadmissible. The experimental method finally adopted in studying the oxidation quantitatively depends on the measurement of the rate of disappearance of oxygen when a suspension of a definite weight of nickel sulphide in a definite volume of water is shaken in contact with this gas.

In conducting an experiment, 0.5 gram of sulphide is introduced into a reaction vessel consisting of a cylindrical tube of about 100 c.c. capacity, into which at opposite ends are sealed glass tubes. One is connected to the gas burette. Through the other, which can be closed with a rubber stopper, 40 c.c. of water or catalyst solution are added. The reaction vessel, which is connected to a jacketed gas burette and immersed in a thermostat, can be rocked longitudinally. A rapid current of oxygen from a cylinder is passed through the apparatus until the reaction vessel and burette are full of this gas. The reaction vessel is then closed, and after allowing about five minutes for the attainment of thermal equilibrium, the gas burette is levelled, the shaker started, and the absorption followed from gas burette readings from time to time. The temperature of the oxygen in the burette is kept constant by circulating through a jacket water from the thermostat.

A fairly slow rate of rocking gave the best agitation, but the oxygen absorption was independent of the rate of agitation above a certain very low rate.

In the adsorption experiments, the procedure was repeated, but at the end of thirty minutes the sulphide was allowed to settle

and the concentration of vanadium estimated by oxidation with permanganate and titration with ferrous sulphate solution, using an electrometric determination of the end-point. The method of Conant (*J. Amer. Chem. Soc.*, 1916, **38**, 341) was modified slightly by titrating in 20 per cent. hydrochloric acid at room temperature.

For the work on the nature of the reaction product, the experiment was carried out in the usual way for some time. The shaker was then stopped, the gas level quickly read, and the contents of the reaction vessel were poured through a filter under suction and washed rapidly with cold water. Excess of ammonia was added and after filtration the nickel was estimated in the customary manner with dimethylglyoxime.

The reaction might conceivably take place in two ways:

- (a) By solution of nickel sulphide followed by oxidation.
- (b) Heterogeneously by direct action of dissolved oxygen upon the solid sulphide.

If the former be the case, the extent of oxidation after a certain time will be independent of the amount of solid sulphide present, whereas if the reaction is heterogeneous the reaction velocity will be proportional to the surface of the sulphide or to the amount of the latter.

This point was investigated by suspending different amounts of a rather active β -sulphide in aerated water and estimating the amount of nickel-ion in solution after a definite time. The following figures (grams) show the reaction to be heterogeneous.

TABLE I.

Amount of NiS	0.1	0.2	0.4
Soluble Ni found	0.0123	0.0241	
" "	0.0121	0.0235	0.043
Amount of NiS		0.2	3
Soluble Ni found		0.0201	0.0289
" "		0.0198	0.0285

Temperature Coefficient.—Measurements were carried out at 25°, 35°, and 45°. The results are expressed as cubic centimetres of oxygen absorbed per hour by 1 gram of nickel sulphide.

TABLE II.

Temperature	25°	35°	45°
γ -Sulphide	2.0	4.0	7.6
β -Sulphide	5.6	12.0	28.4

A temperature coefficient is thus obtained of 2.0 and 1.9 per 10° temperature rise, for the γ -sulphide and 2.15 and 2.37 for the β .

Reaction Product.—A series of experiments was carried out to

test whether the course of the reaction was modified by different concentrations of catalyst. The sulphide was shaken in each case till an approximately equal amount of oxygen had been absorbed. The amount of nickel sulphate in solution was then estimated by the glyoxime method. It will be noticed that the amount of oxygen equivalent to the soluble nickel is greater than the observed oxygen absorption in the case of the stronger catalyst concentrations. This may be attributed to solution by acid produced by the hydrolysis of the catalyst, vanadyl sulphate, of nickel oxide or basic sulphate which is unavoidably formed in washing the precipitated sulphide.

TABLE III.

Concentration of catalyst in millimoles per litre.	C.c. of O ₂ absorbed.	Gram of nickel glyoxime precipitated.	Gram of soluble nickel.	C.c. of O ₂ equivalent to Ni reckoned as sulphate.
0	7.9	0.019	0.00356	2.0
0.96	8.0	0.048	0.00975	7.3
2.4	7.5	0.080	0.0162	12.1
4.8	7.9	0.090	0.0182	13.6
9.6	8.5	0.107	0.0217	16.3
19.2	7.9	0.118	0.024	18.0

Parallel reaction velocity experiments were then carried out in which both the variation of oxygen absorption and the amount of soluble nickel produced were determined. The difference in columns 2 and 5 (Table IV), which is shown in column 6, is fairly constant and corresponds with the amount of soluble nickel produced by solution of the oxide or basic sulphate.

TABLE IV.

4.8 Millimoles of catalyst per litre.

Hours.	C.c. of O ₂ absorbed.	Nickel gly-		O ₂ equiv. to sol. Ni.	Diff.
		oxime found.	Soluble Ni.		
0.25	2.4	0.0570	0.0116	8.6	6.2
0.50	3.85	0.0660	0.0134	10.0	6.15
1.50	7.9	0.0905	0.0182	13.6	5.7
2.75	14.25	0.1385	0.0282	21.0	6.75

The following figures make clear the fact that the product of the reaction is really nickel sulphate and that the apparent variations of Table III are due to an extraneous factor which is eliminated after the first half hour or so. For three concentrations of catalyst, two simultaneous oxidations were carried out. The first was stopped after a short time, the second was allowed to continue for a longer period. In each case, the amount of oxygen absorbed and the soluble nickel produced were estimated. The

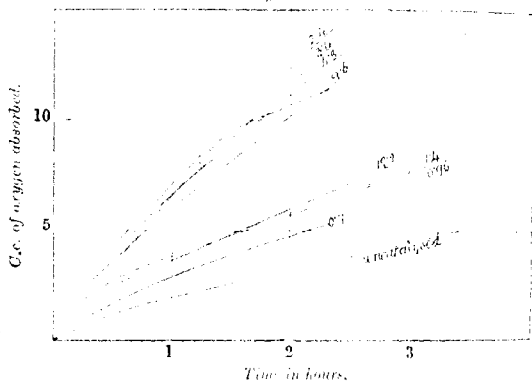
agreement between the amount of oxygen absorbed with the nickel sulphate produced is shown in the third line for each set of determinations.

TABLE V.

Conc. of catalyst.	C.c. of O ₂ absorbed (aver.).	Nickel gly. oxime (gram).	Soluble Ni (gram).	C.c. of O ₂ present as sulphate.	
2.4 millimoles per litre	7.5 119.1	0.0800 0.1440	0.0162 0.0292	12.1 21.8	
Difference		11.6			9.7
4.8 millimoles per litre	3.85 114.25	0.0060 0.1385	0.0134 0.0282	10.0 21.0	
Difference		10.40			11.0
9.6 millimoles per litre	8.5 114.3	0.1070 0.1461	0.0217 0.0296	16.2 22.1	
Difference		5.8			5.9

FIG. 1.

Absorption of oxygen under the influence of varying strengths of catalyst solution.



In Fig. 1 are shown the reaction velocity curves for the catalytic oxidation of nickel sulphide with various concentrations of catalyst. Fig. 2 represents the effect of addition of acid to a solution containing 0.72 millimole of catalyst per litre. The figures by the curves refer to the concentration, in millimoles per litre, of the catalyst and of the acid, respectively.

From these curves the figures tabulated below are obtained and these results are expressed graphically in Fig. 3, which also shows the adsorption of vanadium-ion from solutions of vanadyl sulphate of varying strengths.

FIG. 2.

Absorption of oxygen with fixed catalyst concentration but varying acid concentrations.

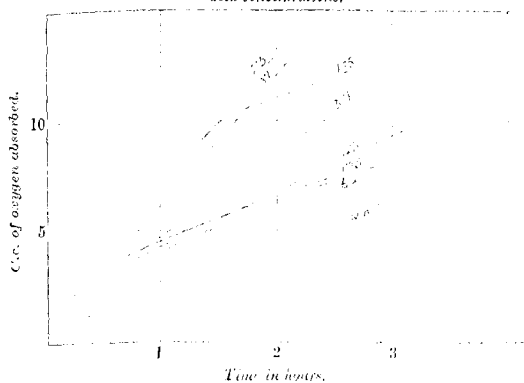
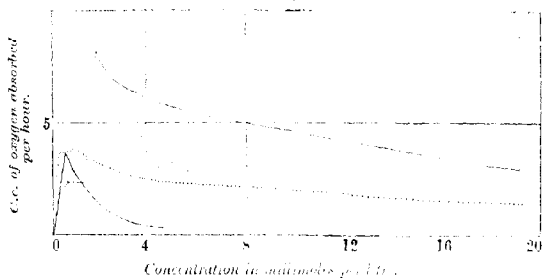


FIG. 3.



- Rate of oxidation of β -NiS at 25° with varying catalyst concentrations.
 ——— Adsorption of vanadium on NiS.
 - - - Variation of rate of oxidation on addition of acid to catalysed reaction.
 Variation of rate of oxidation on addition of acid alone.
 - Variation of rate of oxidation with catalyst concentration γ -NiS at 35°.

TABLE VI.

Rate of absorption of oxygen with varying catalyst concentration.

c = concentration of catalyst in millimoles per litre.

v = reaction velocity. C.c. of oxygen absorbed per hour by 0.5 gram of nickel sulphide.

a	0	0.7	0.96	1.4	1.9	2.4	3.1	4.8	9.6	19.2
b	1.25	1.9	1.9	1.9	6.5	5.6	5.2	4.6	4.15	2.4

U U 2.

TABLE VII.

Rate of absorption of oxygen in presence of sulphuric acid.

Concentration of catalyst = 0.7 millimole per litre.

 a = concentration of acid in millimoles per litre. b = reaction velocity.

a	0	1.25	1.85	2.5	3.1	3.7	4.3	6.2
b	1.9	1.9	6.3	6.3	5.9	3.8	2.5	2.3

TABLE VIII.

Influence of addition of acid on the uncatalysed reaction.

 a = concentration of acid in millimoles per litre. b = reaction velocity. C.e. of oxygen absorbed per hour by 0.5 gram of nickel sulphide.

a	0	3.1	3.7	4.3	6.2
b	1.25	2.3	2.7	2.7	2.4

TABLE IX.

Adsorption of vanadium on nickel sulphide.

 a = concentration of vanadyl sulphate in millimoles per litre. b = mg. of vanadium adsorbed on 0.5 gram of nickel sulphide.

a	0.48	0.72	0.96	1.4	2.4	4.8
b	0.92	1.46	1.18	0.67	0.44	0.12

Discussion of Results.

The discrepancy between the oxygen absorbed and the nickel found as sulphate indicates clearly that the uncatalysed oxidation of moist nickel sulphide proceeds according to Pavia's scheme of a two-stage reaction. The catalytic oxidation, from the fact that sulphate is the product of oxidation, proceeds apparently in one stage. The uncatalysed reaction, however, doubtless proceeds at the same time, and in the case of the catalytic oxidation of a very reactive sulphide traces of sulphur were found at the end of the reaction.

The curves showing the relationship between oxygen taken up and time are approximately linear for the uncatalysed reaction, and this also holds after a short curved portion for the catalytic oxidation of less reactive specimens of nickel sulphide. The curvature in the case of the more reactive sulphides is very distinct and is most noticeable for small catalyst concentrations. The curves showing the relation between catalyst concentration and reaction velocity present unusual features. At first only a very slight increase is observed, but this is followed by a sudden rapid rise to a maximum, after which the reaction velocity falls off more gradually, being roughly a linear function of the logarithm of the concentration. The adsorption curves are also abnormal, for they too, after rising linearly with concentration, suddenly fall off,

although much more rapidly. The form of this curve suggests the intervention of a third factor besides vanadium and nickel sulphide, and it is not unreasonable to suppose that the same inactivating agent was operative in suppressing both catalytic activity and adsorption.

It has been shown (Table III) that, for catalytic oxidation, initially more nickel sulphate is formed than can be accounted for on the ground of oxygen absorption alone, and this excess increases at first rapidly from a negative quantity for zero catalyst concentration up to the concentration of maximum catalytic activity and then more slowly with greater concentrations.

Marked catalytic effect is always associated with a colour change, the bright blue of the vanadyl-ion giving place to the yellow or green characteristic of tervalent vanadium salts. This yellow or green solution is quite stable in presence of oxygen, but the addition of excess of dilute acid restores the blue vanadyl colour when the mixture is shaken with air. Salts of tervalent vanadium are known to be extensively hydrolysed in dilute solution, and it appeared probable that free acid produced by hydrolysis was the disturbing factor. Accordingly, the effect of addition of sulphuric acid, both on the catalysed and uncatalysed reaction, was investigated.

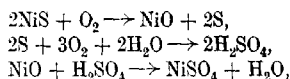
The curve (Fig. 3) showing the influence of acid on the uncatalysed reaction indicates a definite acceleration to a maximum velocity which is followed by a subsequent decrease. The variation, however, is not great, and may be attributed to change in the condition of the sulphide surface. The curve showing the variation of the catalytic reaction velocity with increasing amounts of acid recapitulates all the features of the catalyst concentration curve, although owing to the direct introduction of acid the descending portion is much more compressed.

At the point of optimum acidity, reduction of the catalyst concentration to 0.23 millimole per litre had no effect on the rate of oxygen absorption, which remained constant at 6.3 c.c. per hour.

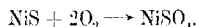
The descending branches of the curves for varying catalyst and for varying acid concentrations are associated with the blue colour of the vanadyl-ion, the flocculation and rapid settling of the nickel sulphide. Semi-quantitative experiments on the time of settling of a suspension of nickel sulphide indicated a maximum stability of the suspension in the neighbourhood of the optimum acid and catalyst concentrations.

The phenomena observed may be accounted for in the following general terms:

There are two distinct modes of formation of nickel sulphate by oxidation:



and the catalytic reaction



The second reaction may be prevented by the presence of a film of nickel oxide, which can, however, be removed by excess of acid produced by hydrolysis of vanadium sulphates or directly introduced.

The catalytic agent is trivalent vanadium, probably in the form of colloidal V(OH)_3 . This is assumed to take up a molecule of oxygen, giving momentarily a quinquevalent vanadium compound, which reacts at the surface of the nickel sulphide, regenerating trivalent vanadium. When the concentration of acid in the system is such that it can keep the nickel sulphide surface reasonably clear and yet is not sufficient either to flocculate the nickel sulphide or to stabilise the vanadyl salt, V^{IV} or VO^{II} , a maximum catalytic effect is observed.

Trillat (*Compt. rend.*, 1903, **137**, 922; 1904, **138**, 94, 274) has observed that whilst neutral manganese salts are almost inactive the addition of a small quantity of alkali renders them catalytically active in promoting the oxidation of certain phenolic substances. In this connexion it is noteworthy that the oxidation potential of the various manganese compounds are strongly influenced by hydrogen-ion concentration. Thus the oxidation potential of a neutral 0.1M-permanganate solution is 1.31 volts, whilst in normal acid it is 2.12 volts. Again, the free energy of the permanganate-manganese reaction is expressed by

$$A = -RT \log k = -\frac{RT}{4} \log \frac{[\text{Mn}^{\text{IV}}] p_{\text{O}_2}^{\frac{1}{2}}}{[\text{MnO}_4^-][\text{H}^+]^2}.$$

Similar data are not available for vanadium, but it appears probable that here again the oxidation potentials, catalytic activity, and hydrogen-ion concentration are intimately connected.

For a solution containing 1.9 millimoles of vanadyl sulphate per litre and for one containing 1.85 millimoles of sulphuric acid an initially rapid oxidation of 6.3 c.c. of oxygen absorbed per hour falls off suddenly to 2.2 and 1.8 c.c. per hour, respectively. Two curves for the oxidation of a β -sulphide at 35° show a similar behaviour. In these cases, one must assume that the uncatalysed reaction still continues to produce nickel oxide, which is progressively removed by slight excess of acid. Eventually, however, all the acid is used up and a protective film of oxide is formed which

diminishes the reaction velocity to the observed low uncatalysed velocity.

In Fig. 3 the behaviour of a specimen of inactive γ -sulphide is shown. It will be noted that the peak of maximum oxidation is at a lower concentration than in the case of the more reactive β -sulphide. This is in accordance with the theory which requires the solution of the oxide film by acid before catalytic oxidation is possible, since the less reactive the sulphide the less nickel oxide is formed in washing and the smaller the quantity of acid required for its removal.

Summary.

The velocity of oxidation of the β - and γ -forms of nickel sulphide in aqueous suspension have been determined by measurement of their oxygen absorption. The oxidation is shown to be a heterogeneous surface reaction, with temperature coefficient in the neighbourhood of 2.

The intermediary formation of basic salts is shown to occur, supporting the hypothesis of a two-stage oxidation process.

The oxidation is markedly accelerated by soluble vanadium salts, which are adsorbed and give nickel sulphate without the intermediary formation of basic salts. The catalytic effect is ascribed to colloidal $V(OH)_3$ and is greatest in weakly acid solutions.

One of us (J. S. D.) wishes to express his indebtedness to the Executive of the Department of Scientific and Industrial Research for a grant which enabled him to carry out this work.

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Received, March 28th, 1923.

CXLV.—The Combustion of Complex Gaseous Mixtures. Part II. Mixtures of Carbon Monoxide and Hydrogen with Air.

By WILLIAM PAYMAN and RICHARD VERNON WHEELER.

By means of the "law of speeds" (see Part I of this research, T., 1922, **121**, 363; also T., 1919, **115**, 1436, 1446, 1454; 1920, **117**, 48), it is possible to calculate the speed of the uniform movement of flame in any mixture of air with a complex inflammable gas mixture, provided that the speeds of the flames in mixtures with air of each of the inflammable gases taken singly is known.

A complexity arose when dealing with mixtures containing carbon monoxide, for the speed of propagation of flame in a given mixture of carbon monoxide with air or oxygen is dependent on

the degree of saturation with water vapour. This fact was established by Dixon (*Phil. Trans.*, 1893, **184**, 97) with regard to the speed of the explosion-wave in the mixture $2\text{CO} + \text{O}_2$, thus:

Condition of mixture.	Water vapour, per cent. by volume.	Speed of explosion-wave in m. per sec.
Well dried	—	1264
Dried	—	1305
Saturated at 10°	1.2	1676
Saturated at 20°	2.3	1703
Saturated at 35°	5.6	1738
Saturated at 45°	9.5	1693

The proportion of water vapour that had the optimum effect on the speed was thus found to lie between 5.6 and 9.5 per cent., and any excess over this quantity retarded the explosion-wave.

Similarly, as regards the uniform movement of flame, it was found (T., 1919, **115**, 1454) that but slight variations in the quantity of water vapour present in mixtures of carbon monoxide and air caused marked changes in its speed.

Some doubt therefore existed as to the correct value to use for the speed of flame in mixtures of carbon monoxide and air when attempting to calculate, by means of the law of speeds, the speed of flame in a complex mixture containing carbon monoxide, unless the degree of saturation of the mixture by water vapour was known.

Dixon has also shown, however (T., 1886, **49**, 94), that hydrogen or any gas containing hydrogen (such as methane) affects the combustion of carbon monoxide in the same manner, and possibly in a similar degree, as does water vapour. It is reasonable to suppose, therefore, that the speed of flame in complex mixtures containing more than a certain small proportion of hydrogen (or of a gas containing hydrogen) in addition to carbon monoxide will be unaffected by the presence of varying quantities of water vapour, since the presence of the hydrogen will ensure that the maximum rate of combustion of the carbon monoxide shall be attained.

Experimental values for the speeds of flame in mixtures of carbon monoxide, hydrogen, and air, in which the carbon monoxide and hydrogen are in a known ratio, should therefore be satisfactory for calculating the speeds of flame in other mixtures in which the carbon monoxide and hydrogen bear a different ratio to each other, so long as the requisite minimum quantity of hydrogen is exceeded. Or the "effective" speeds for mixtures of carbon monoxide and air alone could be calculated from such values, and these speeds used for further calculations, the "effective" speed of flame in a given mixture of carbon monoxide and air, as determined from experiments with mixtures containing more than a certain quantity of hydrogen, being, presumably, that which would be obtained with the optimum saturation of water vapour.

For when flame travels in a mixture of hydrogen, carbon monoxide, and air the effect of the hydrogen may be presumed to be twofold; it will determine the combustion of the carbon monoxide, and it will, by its own combustion, aid in the propagation of the flame. These two effects of the hydrogen can be regarded as independent of each other.

The speeds of the uniform movement of flame, in a horizontal glass tube 2.5 cm. in diameter, in mixtures of air with mixtures of carbon monoxide and hydrogen corresponding in composition with $3\text{CO} + \text{H}_2$ and $\text{CO} + \text{H}_2$, have been determined. The maximum speed of uniform movement of flame in any mixture of $3\text{CO} + \text{H}_2$ and air is 214 cm. per second; in any mixture of hydrogen and air, under the same conditions of experiment, it is 485 cm. per second (Haward and Otagawa, T., 1916, 109, 83). From these two values the maximum "effective" speed in mixtures of carbon monoxide and air can be calculated and is found to be 125 cm. per second. Using this result to calculate the maximum speed of flame in mixtures of $\text{CO} + \text{H}_2$ and air, a value 305 cm. per second is obtained. The measured speed was 315.2 cm. per second.

It should be possible to check the value calculated for the "effective" speed of flame in mixtures of carbon monoxide and air by actual measurement, using mixtures saturated with water vapour at different temperatures. Two series of determinations of this character, the experimental difficulty attending which is considerable, have been made for us by Mr. W. Shepherd.

Two mixtures of carbon monoxide and air were prepared in large gas-holders over water, one containing 45 per cent. of carbon monoxide, this being within the range of mixtures in which the speed of the uniform movement of flame is fastest; and the other 40 per cent. The gas-holders, explosion-tube (a glass tube 2.5 cm. in diameter and 4 m. long), and recording apparatus were installed in a room which could be maintained at a constant temperature and the following records were obtained:

TABLE I.
The Effect of Water Vapour on the Speed of Uniform Movement of Flame in Mixtures of Carbon Monoxide and Air.

Carbon monoxide 45 per cent.			Carbon monoxide 40 per cent.		
Temp. of saturation.	Water vapour per cent. by volume.	Speed in cm. per second.	Temp. of saturation.	Water vapour per cent. by volume.	Speed in cm. per second.
25	0.70	55.5	4 ²	0.80	56.0
13	1.45	76.0	12	1.35	68.2
27	2.50	105.6	20	2.30	85.7
34	5.20	120.0	27	3.50	95.9
42	8.00	118.0	34	5.20	107.4
			39	6.85	106.5

U G*

If these results are plotted as speed-percentage graphs, it will be seen that the effect of water vapour on the speed of the flame tends towards a maximum when about 6.0 per cent. is present. The highest value recorded for the speed of flame in the mixture containing 45 per cent. of carbon monoxide (which is a "maximum-speed mixture")* was 120 cm. per second, which agrees closely with the calculated value for the effective speed, namely 125 cm. per second.

We have suggested that this "effective" speed of propagation of flame in mixtures of carbon monoxide and air is also obtained when more than a certain proportion of hydrogen is present; the question arises as to the least proportion of hydrogen necessary. We have attempted to determine this by measuring the speed of uniform movement of flame in mixtures of carbon monoxide and air containing a small proportion of hydrogen, with and without water vapour.

In the first series of experiments, the mixtures contained varying proportions of water vapour, obtained by saturation at different room-temperatures, and a rough approximation can be obtained from them to the minimum proportion of hydrogen that is equivalent in its effects (on the speed of uniform movement of flame in mixtures of carbon monoxide and air) to water vapour. The experiments were made in a glass tube 2.5 cm. in diameter and 4 m. long.

TABLE II.

The Effect of Hydrogen and of Water Vapour on the Speed of Uniform Movement of Flame in Mixtures of Carbon Monoxide and Air.

Experiment No.	Temperature.	Carbon monoxide per cent.	Hydrogen per cent.	Water vapour per cent.	Speed of flame in cm. per second.
1	6	39.25	0.65	0.90	75.5
2	28	38.00	0.65	3.70	103.5
3	4	39.70	1.90	0.80	103.5
4	6	46.15	3.85	0.90	152.0
5	10	47.30	4.05	1.20	150.0
6	20	46.00	4.05	3.95	167.0
7	20	47.30	4.15	2.30	144.0
8	5	37.45	5.60	0.85	170.0
9	6	43.75	5.60	0.90	170.5
10	31	42.20	5.60	4.40	156.0
11	6	40.80	6.05	0.90	160.5
12	27	39.60	6.05	3.50	158.0

Considering first the mixtures of which the carbon monoxide content was about 40 per cent., and comparing the results obtained

* The phrase "maximum-speed mixture" is used to describe shortly a mixture of inflammable gas and air (or oxygen) in which the proportions of inflammable gas are such that the speed of uniform movement of flame in the mixture, under given experimental conditions, is the fastest obtainable.

with those recorded in Table I, it becomes apparent that more than 1.90 per cent. of hydrogen is required to procure the "effective speed" of uniform movement of flame in these mixtures; whilst with the mixtures containing about 45 per cent. of carbon monoxide, it appears that less than 3.85 per cent. of hydrogen suffices. We will take between 1.90 and 3.85 per cent. as our first approximation to the quantity of hydrogen necessary (as an alternative to water vapour) to develop the effective speed of flame in mixtures of carbon monoxide and air.

It was considered that a definite result should be obtainable more readily by the use of well-dried mixtures, provided that no attempt was made to secure such extreme dryness (of apparatus and contents) as is obtained by their prolonged exposure to the action of phosphoric oxide. That is to say, the presence of a trace of water vapour would be presumed, and slight variations in the amount assumed to be immaterial.

This series of experiments, with well-dried mixtures of carbon monoxide, hydrogen, and air, was based on the fact that when two "maximum-speed" mixtures are mixed, in any proportions, a "maximum-speed" mixture results and the speed of flame in it can be calculated (see T., 1919, **115**, 1452). With carbon monoxide and air, the range of mixtures in which the speed of uniform movement of flame, under given experimental conditions, is fastest contains between 45 and 50 per cent. of carbon monoxide; and with hydrogen and air the range lies between 35 and 40 per cent. of hydrogen. The two mixtures chosen for these experiments contained, respectively, 47.70 per cent. of carbon monoxide and 37.95 per cent. of hydrogen. If these are mixed together in different proportions, so that the resulting complex mixture contains 2.0, 2.5, 3.0, and so on, per cent. of hydrogen, it should be possible to determine, within narrow limits, what percentage of hydrogen, independently of water vapour, is required to cause the flame in a mixture of carbon monoxide and air to assume its "effective" speed; for until the requisite quantity of hydrogen is present the observed speed of flame in the complex mixture will be less than that calculated, since the effective speed of flame in the mixture of carbon monoxide and air is used in the calculation.

The experimental mixtures, prepared by blending the maximum-speed mixtures, were stored in glass gas-holders over dilute potassium hydroxide solution, and were passed slowly through a series of drying-tubes, containing calcium chloride, and Winkler worms, containing concentrated sulphuric acid, into the glass explosion-tube (2.5 cm. in diameter and 4 m. long), which was dried before each experiment by washing with pure alcohol and ether and

heating in a current of dried air. At the outset of the series of experiments, when the mixtures used contained less than 3.0 per cent. of hydrogen, the speed of flame in a mixture of given composition was not constant, and it became apparent that but slight variation in the magnitude of the "trace" of water vapour present affected the results. For example, with a mixture containing carbon monoxide 44.20 and hydrogen 2.30 per cent., the following results were obtained for the speed of uniform movement of flame, as measured by the fusion of screen-wires (T., 1914, **105**, 2610): 93.9, 101.9, 105.9, 97.8, 109.1, 112.2, and 119.2 cm. per second. Prolonged drying of this mixture rendered it incapable of being ignited by the means normally employed in the experiments.

Evidence having been obtained that the speed of the flame was not always strictly uniform—it appeared sometimes to increase as the flame travelled from the open to the closed end of the tube—recourse was made to the photographic method of registration of speed (T., 1919, **115**, 579), using a tube of "Uviol" glass, and a quartz lens. It then became clear that, unless the proportion of hydrogen present exceeded 3.0 per cent., there was, instead of a uniform speed, an acceleration of speed as the flame travelled away from the point of ignition (see Fig. 1). Considerable care was taken during these later experiments of the series to secure the same degree of dryness of the mixtures, and it was observed that any deviation from the usual procedure that would tend to increase the efficiency of removal of moisture rendered the mixtures incapable of propagating flame: the flame would burn during a few seconds at the mouth of the tube, owing no doubt to the mingling of moist air with the mixture, but would not travel along it. Moreover, with the normal conditions of drying used in these experiments, flame would not propagate if less than 2.0 per cent. of hydrogen were present, whereas with a slight increase in the amount of moisture flame travelled readily in such a mixture.

Apparently, then, moisture is more effective than hydrogen in promoting the combustion of carbon monoxide.

The results obtained for the speeds of flames in the blended maximum-speed mixtures of carbon monoxide and air and hydrogen and air, dried by exposure to calcium chloride and sulphuric acid, are shown in Table III.

From these results it is evident that the presence of 2.95 per cent. of hydrogen is nearly, if not quite, sufficient to enable the uniform movement of flame in a mixture of carbon monoxide and air to acquire its "effective" speed, whereas less than that quantity is insufficient.

This minimum quantity of hydrogen, which can be stated to be,

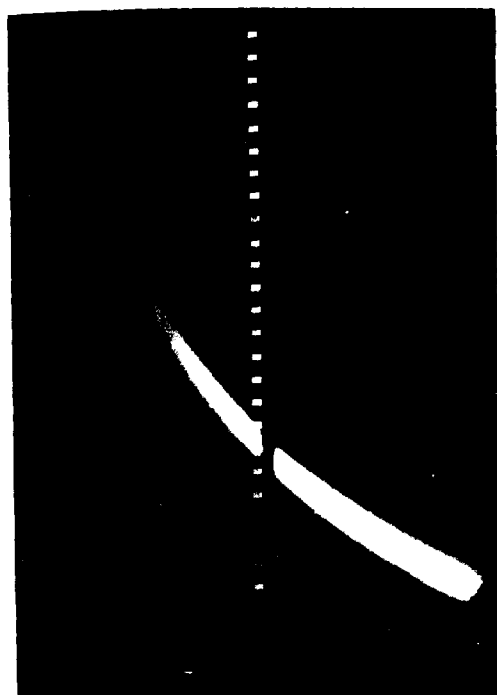


FIG. 1

(a)

TABLE III.

Experiment No.	Carbon monoxide per cent.	Hydrogen per cent.	Speed of uniform movement of flame in cm. per second.	
			Observed.	Calculated.
1a	34.75	9.40	213	202
2a	40.55	5.85	171	170
3a	43.30	3.70	156	156
4a	43.80	2.95	146	147
5a	43.40	2.45	130	144
6a	43.65	2.25	123	142

in round numbers, 3 per cent., should be compared with the optimum quantity of water vapour required to enable the uniform movement of flame in mixtures of carbon monoxide and air to assume its maximum speed, namely, about 6 per cent. Whence it would appear that, whereas a trace of water vapour is more effective than a trace of hydrogen in enabling propagation of flame to take place in dried mixtures of carbon monoxide and air, twice as much of it is required to give to that propagation its complete freedom.

Inflammation in a Closed Vessel.

The "law of speeds" can be shown to apply to conditions of propagation of flame other than the "uniform movement," provided that the conditions of experiment are constant. For example, the speeds of flame in complex gaseous mixtures enclosed in a spherical vessel obey the law closely.

A series of experiments with mixtures of carbon monoxide, hydrogen, and air illustrative of this may be recorded here, since they also serve to emphasise the necessity, when attempting to interpret the results, for deducing the "effective" speed of flame in mixtures of carbon monoxide and air when that gas is a constituent of a complex gaseous mixture.

For these experiments a spherical explosion vessel of brass, of 4 litres capacity, was used, and a spark-gap, 1 cm. long, at which ignition of the mixtures was effected by a secondary discharge from an induction-coil, was formed between pointed electrodes at the centre of the sphere. Measurements of the pressure produced on inflammation of the mixtures, and the rate of development of that pressure, were recorded by means of a Petavel gauge with photographic registration, specially designed to enable the comparatively low pressures developed (6 or 7 atmospheres) to be recorded accurately; and the time of passage of the secondary discharge that caused ignition was recorded on the same photographic film, together with the record of a tuning-fork having 50 vibrations per second.

It has been shown (T., 1918, 113, 851) that the time taken for the pressure within a spherical vessel to attain its maximum

(ignition of the mixtures being at the centre), measured from the time of passage of the electric spark that causes ignition, coincides with the time taken for flame to reach the boundary of the vessel, except with very slowly moving flames. In the discussion of the results that follows, therefore, the time of attainment of maximum pressure is taken to be synonymous with the time of passage of flame from the centre to the sides of the vessel, a distance of 9.85 cm.; whence calculation can be made of the mean speeds of the flames.

The series of experiments was carried out with mixtures, in different proportions, of air with carbon monoxide, hydrogen, and complex mixtures corresponding with $3\text{CO} + \text{H}_2$, $\text{CO} + \text{H}_2$, and $\text{CO} + 3\text{H}_2$. The initial temperature and pressure of each mixture were atmospheric and each was saturated with water vapour at room temperature (15°). A discussion of all the results obtained both as regards pressures developed and speeds of flame, will form the subject of another communication; we are here concerned only with the speeds of the flames in the "maximum-speed" mixtures. These are recorded in Table IV.

TABLE IV.
Mean Speeds of Flames in Maximum-speed Mixtures in a Closed Vessel.

Combustible gas.	Time, in seconds, between ignition and attainment of maximum pressure.		Mean speed of flame in cm. per second.	
	Observed.	Calculated.	Observed.	Calculated.
Carbon monoxide	0.0670*	—	146	—
$3\text{CO} + \text{H}_2$	0.0296	0.0282	340	345
$\text{CO} + \text{H}_2$	0.0230	0.0230	428	428
$\text{CO} + 3\text{H}_2$	0.0190	0.0194	518	511
Hydrogen	0.0168	—	595	—

* The calculated "effective" time is 0.0638 sec.

† The calculated "effective" speed is 261 cm. per sec.

The agreement between the calculated and the observed values is exceedingly close, showing that the law of speeds holds equally well for propagation of flame within a closed sphere as it does for the "uniform movement."

Further information is obtainable respecting the applicability of the law of speeds from the work of Bone and Haward (*Proc. Roy. Soc.*, 1921, **100**, 67) on the combustion of mixtures of hydrogen-carbon monoxide, and air at high initial pressures. There is recorded in their paper, for a number of mixtures, the time taken for the attainment of maximum pressure; we have used these results for our calculations, which are given in Table V. From the results recorded for the two mixtures $2\text{H}_2 + \text{O}_2 + 4\text{N}_2$ and $1.12\text{H}_2 +$

$23/12\text{CO} + \text{O}_2 + 4\text{N}_2$ the "effective time" for the mixture $2\text{CO} + \text{O}_2 + 4\text{N}_2$ is found to be 0.038 sec.

TABLE V.

Gaseous Combustion at High Pressures (Bone and Haward).

Mixture.	Observed.		Calculated.	
	Time in sec.	Reciprocal of time, Relative speeds of flames.	Time in sec.	Reciprocal of time, Relative speeds of flames.
(1) $2\text{H}_2 + \text{O}_2 + 4\text{N}_2$	0.065	200	—	—
(2) $\text{H}_2 + \text{CO} + \text{O}_2 + 4\text{N}_2$	0.015	66.6	0.009	111.1
(3) $\frac{1}{2}\text{H}_2 + 3/2\text{CO} + \text{O}_2 + 4\text{N}_2$	0.015	66.6	0.014	71.4
(4) $\frac{1}{3}\text{H}_2 + 7/4\text{CO} + \text{O}_2 + 4\text{N}_2$	0.025	40	0.021	47.6
(5) $\frac{1}{4}\text{H}_2 + 11/6\text{CO} + \text{O}_2 + 4\text{N}_2$	0.025 to 0.030	40 to 33.3	0.025	40
(6) $\frac{1}{5}\text{H}_2 + 23/12\text{CO} + \text{O}_2 + 4\text{N}_2$	0.030	33.3	0.030	33.3
(7) $2\text{CO} + \text{O}_2 + 4\text{N}_2$	0.180	5.6	—	—

We consider that our results are best explained by the hypothesis advanced by Dixon before the British Association in 1880 to account for the fact that a mixture of carefully dried carbonic oxide and oxygen would not explode when electric sparks were passed through it, but that on the addition of a minute trace of water, or volatile substance containing hydrogen, the mixture became inflammable; the hypothesis being that the steam acts the part of a "carrier of oxygen" by undergoing reductions and successive reformations.

There seems little doubt but that the considerations we have advanced regarding the "effective speed" of combustion of carbon monoxide, which is obtained when more than a certain small proportion of hydrogen or of water vapour is present, are applicable also to the propagation of flame by the detonation-wave. Professor Dixon informs us that the speed of the detonation-wave in mixtures of carbon monoxide, hydrogen, and oxygen is such that by extrapolation the value for the "effective" speed in the mixture $2\text{CO} + \text{O}_2$ is 1740 m. per second; which is the same (1738 m. per second) as the speed he obtained when the mixture $2\text{CO} + \text{O}_2$ was saturated with water vapour at 35°, the proportion of water vapour then present being that which had the optimum effect on the speed of the detonation-wave in that mixture. In this connexion it is of interest to recall the experiments of Berthelot (*Ann. Chim. Phys.*, 1881, [v], 28, 289), whereby he showed that the measured rate of the detonation-wave in mixtures of carbon monoxide and oxygen alone was about half its theoretical value, whereas when hydrogen was present in the mixture the calculated values were in good agreement with those found.

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[Received, February 14th, 1923.]

CXLVI.—*The Influence of Nitro-groups on the Reactivity of Substituents in the Benzene Nucleus. Part VII. Reactions of 2:5- and 4:5-Dinitro-m-xylenes.*

By KATHLEEN IBBOTSON and JAMES KENNER.

ANY measure of success which has attended the investigations described in this series of papers must be attributed to the adoption at the outset of Flürscheim's theory of alternate weak and strong linkages in carbon chains as a basis of explanation. Conversely, it may be claimed that this or any other theory which suggests the existence of such an alternating condition in carbon chains is supported by the results in question. As, however, there is a variety of such theories at the present time, some comparative discussion of them in relation to the mobility of substituents in the benzene nucleus seems desirable.

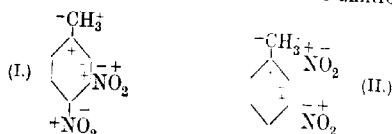
The newer electrical theories agree in attributing the alternating effect to successive variations in polarity of the chain of atoms composing the molecule, but differ in what may at first seem a relatively unimportant point. Thus, according to Fry ("The Electronic Conception of Valence," London, 1921), alternation of polarity characterises the molecule at all times, whilst Lapworth (*Mem. Manchester Phil. Soc.*, 1919, 64, iii, 1; *T.*, 1922, 121, 416) and Kermack and Robinson (*T.*, 1922, 121, 427) assume polarity to be developed only when the molecule is in the activated or constrained condition in which it takes part in chemical reactions. Both Lapworth and Robinson have indicated in general terms their dissent from Fry's attitude, but have refrained from any more specific discussion. Since it is with the behaviour of the reacting molecule that chemists are concerned, it might be suggested that a differentiation between the two views is at least immaterial, if not impossible. In our view, this is not so.

Fry's fundamental assumption that two atoms in combination must have opposite electrical charges is negatived by the conception of the sharing of electrons, introduced by Stark (*Jahrbuch Radioaktivität Elektronik*, 1908, 5, 124), and applied by him to all compounds, whether exhibiting electro- or co-valence, as they are termed by Langmuir. According to Langmuir, again, the sharing of electrons (covalence) is the usual mode of combination of the atoms in organic compounds. On the other hand, since Kossel's views (*Ann. Physik*, 1916, 49, 229) accord with the assumptions made by Fry, the latter's view cannot be dismissed solely on the ground indicated. But its practical value is greatly diminished, if

not entirely removed, by its admission of the possibility of electronic tautomerism :

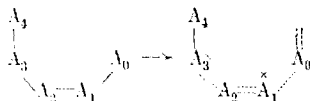


Since Fry, in common with Lapworth and Robinson, associates the behaviour of certain groups with their polarity, uncertainty in this respect must render it impossible to use the theory as a means of predicting the behaviour of a given compound. Granting, however, the possibility of such tautomerism in certain compounds, similar distributions of polarity would at least be expected in closely related compounds, such as, for example, 3:4- and 2:3-dinitrotoluenes.

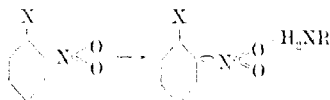


According to Fry's view, the mobility of substituents in the ortho- or para-position to a nitro-group in the benzene nucleus is due to the positive character of the nitro-group. The reactivity of the 3-nitro-group in 3:4-dinitrotoluene would therefore indicate that the 4-nitro-group is positive, as shown in I. It would therefore be anticipated that a similar distribution of polarity would occur in 2:3-dinitrotoluene, as in (II), resulting again in the mobility of the 3-nitro-group. This, however, is not the case, so that Fry's theory is inadequate in this case. On the other hand, Stieglitz (*J. Amer. Chem. Soc.*, 1921, **44**, 1293) has urged very strongly the advantage of the polar over the non-polar (electron-sharing) conception of valency in interpreting the reactions of organic compounds. At the same time, however, he has pointed out that this view can be reconciled with the non-polar conception, if it be assumed that reacting molecules exhibit polar, whilst the normal molecules exhibit non-polar, valency. As already indicated, this is the view independently adopted by Lapworth and Robinson. According to it, the distribution of polarity depends on the particular "key-atom" which is constrained or activated, and so permits the above dilemma to be successfully overcome. Thus, "non-ionic association with other uncharged molecules" is among the possible causes of constraint enumerated by Lapworth (*loc. cit.*, p. 426), and corresponds precisely with the preliminary compound formation upon which one of us has based his conception of the mode of displacement of mobile substituents from the benzene nucleus. In fact, the views referred to constitute a particular case of the application of the theory of induced alternate polarity. This will be the more apparent

when the similarity is observed between the scheme by which Lapworth (*loc. cit.*, p. 416) represents the change ensuing upon a constraint such that the bond between A_0 and A_1 is decreased by the passing of partial valency to the exterior of the system,



and that employed in the first paper of this series (T., 1914, 105, 2722) to portray the first effect of the addition of an amine to an aromatic nitro-compound (compare also Borsche, *Annalen*, 1911 386, 356):



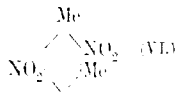
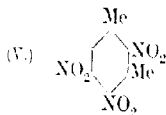
This comparison also illustrates the close relationship between Flürscheim's and the newer theory. Lapworth's scheme is readily seen to contain an alternation of weak and strong linkages, as postulated by Flürscheim, but differently distributed and in the reacting rather than in the normal molecule, to which Flürscheim applied his conception. Apart from this distinction, it would seem that the newer theory in such of its applications as are analogous to those considered above rather includes than supersedes that of Flürscheim. It may be said that each of them leads to the same conclusion in regard to atoms or groups which, according to the former, develop negative polarity, but Flürscheim's theory does not enable the reversal to be foreseen which occurs in the order of reactivity of, for example, the isomeric methoxybenzyl bromides when sodium hydroxide is replaced by hydrogen iodide as the reagent employed (Lapworth and Shoesmith, T., 1922, 121, 1391).

But it will be apparent that the general application of the theory of induced alternate polarity is dependent on a correct choice of the key-atom, and this is not, subject to a reservation which will be indicated, dealt with by the theory as up to the present enunciated. Not only, however, has a particular aspect of the theory of induced alternate polarity been employed throughout this series of papers, but the principles for determining what is now termed the "key-atom" in the type of reaction immediately concerned have been pointed out. Further, these have been vindicated by the experimental evidence subsequently accumulated by Hollman and his collaborators (*Rec. trav. chim.*, 1915, 34, 1: 1920, 39, 434, 480, 736; 1921, 40, 67, 451), and also by the observations of Morgan

and his co-workers (T., 1920, 117, 784; 1921, 119, 187, 1538). Thus, the cases * of 2:3-dinitrotoluene (K), 2:3-dinitrochlorobenzene (H), 2:5-dinitro-1:3-dichlorobenzene (H), 3:4-dinitro-1:2-dichlorobenzene (H), 4:5-dinitro-1:2:3-trichlorobenzene (H), 3:6-dinitro-1:2:4-trichlorobenzene (H), 2:3-dinitroanisole (B), 5:6-dinitro-*o*-chlorotoluene (M), all illustrate the principle that it is the sterically freer of two nitro-groups which takes part in the necessary preliminary compound formation through one of its oxygen atoms, so that this is the key-atom. Another aspect of this consideration is exemplified by the greater reactivity of 4:6- than of 2:4-*m*-dinitrobenzene. In the former case, both nitro-groups, but in the latter, only one is available for the preliminary compound formation.

When various nitro-groups are equally or approximately equally situated in respect of steric conditions, the mobile substituent is that favoured by the directive influence of the majority of the substituents. This directive factor is exactly expressed in terms of polarity as the "tendency to certain molecular distributions of affinity" (Lapworth, *loc. cit.*, p. 426; Kermack and Robinson, *loc. cit.*, p. 432), and is well illustrated by the case of 3:4:6-trichloro-1:2-dinitrobenzene previously discussed (Burton and Kenner, T., 1922, 121, 489). In such a case, an oxygen atom of one of the immobile nitro-groups is the key-atom.

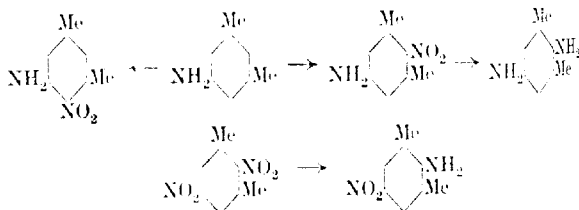
Of the two factors above considered, it will be clear from the examples quoted that the first is the more powerful. Nevertheless, it might be expected that a sufficient accumulation of substituents would enable the directive to overpower the steric factor. This is actually observed in the case of 2:4:5-trinitro-*m*-xylene (V) (Blanksma, *Rcc. trav. chim.*, 1906, 25, 168), in which all the substituents favour the mobility of the 5-nitro-group, but the steric considerations would suggest that the 2- or 4-nitro-group would suffer replacement. It was therefore desirable to examine the behaviour of 2:5-dinitro-*m*-xylene (VI) towards methyl-alcoholic ammonia, since in this case the directive influence of the 4-nitro-group would be lacking, and it might be anticipated that the steric factor would again be in the ascendant.



* The mobile atoms are printed in thick type. The letters in brackets indicate the workers who examined the compound. B = Bantlin, *Ber.*, 1878, 11, 2099; H = Holleman; K = Kenner and Parkin; M = Morgan.

The preparation of 2 : 5-dinitro-*m*-xylene described by Blanksma (*loc. cit.*) proved to be laborious. Partial reduction of 2 : 4 : 6-tri-nitro-*m*-xylene to 2 : 4-dinitro-6-amino-*m*-xylene, followed by the elimination of the amino-group, seemed a more promising mode of obtaining 2 : 4-dinitro-*m*-xylene, to which Blanksma's procedure of reduction, followed by acetylation and nitration, could then be applied. Moderate yields of the desired dinitroxyldine were in fact obtained, although the properties of the base and of its benzoyl derivative differed from those attributed to it by Maltese (*Gazzetta*, 1909, 39, i, 517), who claimed to have prepared it from 2-nitro-benzo-4-*m*-xylide by nitration. Since, however, our product was converted by diazotisation and treatment with alcohol into 2 : 4-dinitro-*m*-xylene, there seems little doubt that Maltese was mistaken in the constitution he assigned to his compounds. Another source of 2-nitro-4-*m*-xylidine was opened up by the discovery of Pearman (*T.*, 1921, 119, 717) that Noelting and Collin (*Ber.*, 1884, 17, 265) had overlooked the formation of this base with its 6-nitro-isomeride during the nitration of 4-*m*-xylidine in presence of sulphuric acid. We are able to confirm this statement, although it should be noticed that, as Mr. Pearman himself informed us, the figures quoted by him as to the proportion of the 2-nitro-derivative produced only refer to incompletely purified material.

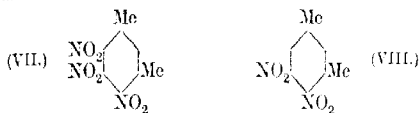
As a further preliminary to the investigation of the action of ammonia on 2 : 5-dinitro-*m*-xylene, the previous preparation of at least one of the two possible, but previously unknown, products was desirable. This was achieved by the fortunate observation, prior to the publication of Pearman's work, that Noelting and Forel (*Ber.*, 1885, 18, 2679) were mistaken in stating that the sole product of the nitration of 5-*m*-xylidine is 4-nitro-5-*m*-xylidine, m. p. 54°. In our experiments, this was accompanied by a considerable proportion of a less soluble isomeride, m. p. 132°, which could scarcely be other than 2-nitro-5-*m*-xylidine, an inference confirmed by reduction of the new base to the known 2 : 5-diamino-*m*-xylene (Noelting and Thiesmar, *Ber.*, 1902, 35, 640):



The action of methyl-alcoholic ammonia on 2 : 5-dinitro-*m*-xylene

took place extremely slowly, even at 200°, and the only basic product isolated melted at 158°. It is therefore clear from the foregoing that its constitution must be that of a 5-nitro-2-*m*-xylydine, and that in this case the steric factor outweighs the opposing directive factor, whilst the reverse is true in the case of 2 : 4 : 5-trinitro-*m*-xylene.

Similarly, although, as the foregoing discussion would indicate, the directive factor determines the behaviour of 4 : 5 : 6-trinitro-*m*-xylene (VII) (Blanksma, *loc. cit.*), it is now shown that in 4 : 5-dinitro-*m*-xylene (VIII) this is not sufficiently powerful to overcome the steric influences, so that in the main the 4-nitro-group is displaced by means of ammonia, although some 4-nitro-5-*m*-xylydine is formed at the same time.



It has previously been remarked that the dinitrotoluenes are less reactive than the chlorodinitrobenzenes towards ammonia, and it is now found that the dinitroxylens are still less reactive than the dinitrotoluenes, owing to the diminished general negative character of the molecule (compare, *inter alios*, Kenner, T., 1914, 105, 2728; Kermack and Robinson, *loc. cit.*, p. 430).

This influence of the general character of the molecule on its reactivity renders caution necessary in comparing compounds which are not isomeric, but the very much greater mobility of the chlorine atoms in 2 : 4-dichloronitrobenzene than in 1 : 3 : 5-trichlorobenzene (compare Holleman, *loc. cit.*, 1920, 39, 736) may probably safely be considered to illustrate the greater efficacy of "non-ionic association with other uncharged molecules" than of "absorption of thermal energy" (Lapworth, *loc. cit.*) as a mode of activating the molecule. For only the nitro-derivative readily forms a molecular compound with the reagent.

The various considerations advanced above also permit a correct pre-estimation as to which are the most and least reactive members of each series of isomerides examined by Holleman and his collaborators. In the simpler cases, this may also be claimed in regard to the intermediate members of each series (compare Kenner and Parkin, *loc. cit.*), but it is not surprising that with the more highly substituted compounds it is difficult correctly to evaluate the relative effects of the various influences which operate. Further, it appears to be too often overlooked that comparisons of different compounds by means of experiments on their velocities of reaction are only strictly legitimate when the determinations are performed

under "corresponding" conditions—using the term with the connotation attributed to it in the Law of Corresponding States. For this reason, it seems probable that while any expected considerable differences will be reflected by such measurements, finer variations will not be correctly reproduced. It is possibly for this reason that 2:3:5-trichloronitrobenzene is unexpectedly somewhat less reactive than the 2:3:4-isomeride, although the 2:4:6-derivative, as would be anticipated, reacts considerably more readily than 2:4:5-trichloronitrobenzene. When a comparison is attempted of one derivative with another derived from it by substitution, not only is the effect of non-correspondence between them likely to be more accentuated, but still further complications are involved in regard to the general character of the molecule. Again, it seems at least doubtful whether it can justifiably be assumed that the substituents common to two compounds make exactly the same contribution to the respective properties of each. For these reasons, it would seem that no very definite conclusion is likely to follow from a study of the ratios of reaction velocities of various compounds, and it is not surprising that the values calculated by Holleman to represent the effect of subjecting the molecules of various compounds to the same modification by substitution show considerable variations.

EXPERIMENTAL.

Nitration of s-m-Xylidine.

A solution of the base (5.5 grams) in sulphuric acid (55 grams) was nitrated at 0° by gradual addition of a mixture of nitric acid (2.88 grams; *d* 1.4) and sulphuric acid (5.77 grams). After two hours, the mixture was poured into water and left for twelve hours. The solution, after removal of oily matter (0.5 gram), was neutralised with ammonia solution. The precipitate immediately formed (2 grams) was separated by fractional crystallisation from benzene and light petroleum (b. p. 70–80°) into a less soluble portion (1.2 grams), m. p. 129–132°, a more soluble portion (0.5 gram), m. p. 56°, and an oily mixture of the two. A further quantity of nitro-base (2.3 grams) separated from the neutralised aqueous solution of the two, and was found to be a mixture from which the two bases just referred to could only be separated with much difficulty.

The base, m. p. 56°, was characterised as 4-nitro-*s-m*-xylidine (Noelting and Ford, *loc. cit.*, quote 54° as the melting point), by the preparation of its *acetyl* derivative, m. p. 114° (Found: N = 13.46. $C_{10}H_{12}O_3N_2$ requires N = 13.46 per cent.).

The less soluble product, finally obtained in the form of orange, rectangular, prismatic crystals, m. p. 132°, was isomeric with the 4-nitro-derivative (Found: N = 16.88. $C_8H_{10}O_2N_2$ requires N =

16.87 per cent.), and therefore was 2-nitro-*s-m*-xyldine. Its *acetyl* derivative separated from dilute alcohol in prisms, m. p. 163° (Found: N = 14.11. $C_{10}H_{12}O_3N_2$ requires N = 13.46 per cent.). With the object of finding further evidence as to the constitution of the base, it was reduced in boiling glacial acetic acid solution by the addition of excess of stannous chloride, dissolved in hydrochloric acid. The product, isolated in the usual manner, was identified as 2:5-diamino-*m*-xylene by its melting point, 191°, and its colour reactions with ferric chloride and with potassium dichromate (compare Noetting and Thesmar, *loc. cit.*).

2:4-Dinitro-6-amino-m-xylene.

The partial reduction of 2:4:6-trinitro-*m*-xylene with ammonium sulphide has been previously studied by Mioti and Lotti (*Gazzetta*, 1897, 27, i, 296), but the object of these investigators was rather the preparation of 2-nitro-4:6-diamino-*m*-xylene than of 2:4-dinitro-6-amino-*m*-xylene. The procedure adopted in the present experiments was based on that applied by Holleman and Böescken (*Rec. trav. chim.*, 1897, 16, 425) to 2:4:6-trinitrotoluene.

A well-stirred suspension of finely ground trinitro-*m*-xylene (10 grams) in alcohol (20 c.c.) was gradually treated at the ordinary temperature with a fresh solution of ammonium sulphide (14 c.c.), prepared by saturating ammonia solution (20 per cent.) with hydrogen sulphide. The product was evaporated to dryness and twice extracted with boiling dilute hydrochloric acid (500 c.c.; *d* 1.055). The acid extract on neutralisation with ammonia solution deposited the base (3 grams in the most favourable cases) in a condition sufficiently pure for the preparation of 2:4-dinitro-*m*-xylene. By crystallisation from dilute acetic acid, it was obtained in amber-coloured, elongated, rectangular prisms, m. p. 193 (Found: N = 29.3. $C_8H_6O_4N_3$ requires N = 19.9 per cent.).

The *acetyl* derivative, prepared by the action of acetic anhydride on the base in the presence of a few drops of sulphuric acid, formed transparent, lozenge-shaped crystals, m. p. 176 (Found: N = 16.88. $C_{10}H_{11}O_5N_3$ requires N = 16.6 per cent.).

The *benzoyl* derivative was readily obtained by the action of benzoyl chloride on the base in the presence of pyridine, and formed colourless, prismatic needles, m. p. 218 (Found: N = 13.47. $C_{15}H_{13}O_5N_3$ requires N = 13.33 per cent.).

Diazotisation of the base in sulphuric acid solution and subsequent treatment with absolute alcohol gave rise to 2:4-dinitro-*m*-xylene, m. p. 82°, and thus established its constitution. It would therefore seem that the statement of Maltese (*loc. cit.*), according to which the base melts at 145° and its benzoyl derivative at 244°, is erroneous.

Action of Ammonia on 2:5-Dinitro-m-xylene.

2:5-Dinitro-*m*-xylene was prepared according to the directions of Blanksma (*loc. cit.*) from 2-nitro-4-*m*-xyldine, the preparation of which base has been discussed in the theoretical part of this paper.

In the initial experiment, the dinitro-derivative (1 gram) was heated with a mixture of ammonia solution (2.3 c.c.; d 0.880) and methyl alcohol (14 c.c.) for twenty-eight hours at 160–210°. Methyl alcohol was removed from the resulting solution by distillation, and the residue extracted with hot concentrated hydrochloric acid. Seventy per cent. of slightly impure, unchanged dinitro-derivative remained undissolved. The quantity of base precipitated by ammonia from the acid extract sufficed for its crystallisation from a mixture of benzene and light petroleum, but not for analysis. Another experiment was therefore performed in which the dinitro-derivative (0.75 gram) was heated with methyl-alcoholic ammonia at 200° for thirty-two hours, until no very noticeable further deepening in colour of the solution occurred. Unchanged material (0.33 gram) was, however, again recovered, the quantity of basic product obtained being 0.26 gram. By crystallisation, this was obtained in orange-yellow needles, *m. p.* 158°. The base depressed the melting point of, but was isomeric with, 2-nitro-3-*m*-xyldine (Found: $N = 17.21$. $C_8H_{10}O_2N_2$ requires $N = 16.87$ per cent.), and therefore was 5-nitro-2-*m*-xyldine. Its acetyl derivative melted at 178°.

Action of Ammonia on 4:5-Dinitro-m-xylene.

4:5-Dinitro-*m*-xylene (3.92 grams) was heated with ammonia solution (5 c.c.; d 0.880) and methyl alcohol (27 c.c.) for fourteen hours at 160°. After removal of the methyl alcohol by distillation, the basic residue was purified by crystallisation from light petroleum, and obtained in red plates, *m. p.* 67–68°, which were identified as 5-nitro-4-*m*-xyldine by direct comparison. The impure base in the mother-liquors was then acetylated. After treatment with steam to remove a small amount of unchanged dinitro-*m*-xylene, the acetyl derivative melted at 171°, and was identified as 5-nitro-4-aceto-*m*-xylylde. By concentration of the aqueous liquors, a small quantity of material was obtained, *m. p.*, after recrystallisation, 105°. This consisted chiefly of 4-nitro-5-aceto-*m*-xylylde, since its mixture with this compound melted at 105–106°.

The authors wish to take the opportunity of thanking Messrs. J. W. Leitch & Co., Ltd., and Mr. S. Pearman for the supply of some of the materials used in this investigation.

THE UNIVERSITY, SHEFFIELD.

[Received, March 7th, 1923.]

CXLVII.—*Nitro-derivatives of m-Cresol.*

By GEORGE PHILIP GIBSON.




IN carrying out certain other investigations, a considerable quantity of 2-nitro-*m*-cresol was required. This compound is not described in the literature, but Khotinsky and Jacopson-Jacopmann (*Ber.*, 1909, 42, 3097) claim to have prepared a crystalline methyl derivative melting at 88°. These authors nitrated *m*-cresol according to Staedel's directions (*Annalen*, 1881, 210, 1259; 1883, 217, 5) and separated the volatile 2- and 4-nitro-*m*-cresols by distillation in steam. According to Khotinsky and Jacopson-Jacopmann, the solid which separated from the cold aqueous distillate was 4-nitro-*m*-cresol,* whilst the aqueous solution contained 2-nitro-*m*-cresol; the latter, obtained as an oil by extracting with ether, and treated with methyl sulphate and alkali, yielded the crystalline methyl derivative melting at 88°.

An examination of Khotinsky and Jacopson-Jacopmann's method showed that, although the yields of 4- and 6-nitro-*m*-cresols were satisfactory, that of the supposed 2-nitro-*m*-cresol was very small; this product, moreover, was found to contain 4-nitro-*m*-cresol, which is slightly soluble in cold water, and up to the present all attempts to prepare from it the crystalline methyl derivative of melting point 88° have been unsuccessful.

As 2-nitro-*m*-cresol could not be prepared by the above process, further experiments were made and it was found that good results were obtained by a method similar to that used by Kauffmann and de Pay (*Ber.*, 1904, 37, 725) for the conversion of resorcinol into 2-nitroresorcinol. *m*-Cresol was first sulphonated, the product was nitrated, and the resulting nitro-*m*-cresolsulphonic acids were hydrolysed with superheated steam at 160—170°. The yield of the yellow oil thus obtained amounted to 80 per cent. of the theoretical, and from it crystalline acetyl, benzoyl, and methyl derivatives were prepared, accompanied in each case by some oily by-product. As the methyl derivative melted at 54°, instead of at 88° as stated by Khotinsky and Jacopson-Jacopmann, and as the methyl derivative of 4-nitro-*m* cresol melts at 62° (*idem*, *loc. cit.*), it was necessary to prepare for direct comparison corresponding derivatives of the known nitro-*m*-cresols (4- and 6-nitro-*m*-cresols). It was thus proved that the nitro-*m*-cresol obtained as indicated above is not identical with either of the known isomerides and is, in fact, as will be shown later, 2-nitro-*m*-cresol.

* 4-Nitro-*m*-cresol is described in Stelzner's "Literatur-Register der organischen Chemie" (1914—15, p. 440, last entry as methyl 3-nitro-2 phenol. Reference to the original paper shows that the compound is 2-nitro-*m*-cresol, which is incorrectly styled by the compiler of the Register.

The more important properties of these compounds are given in the following table.

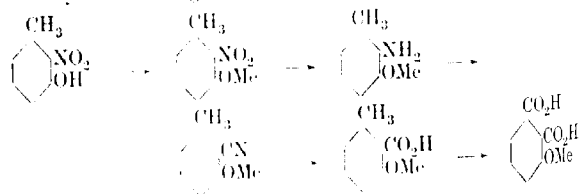
Derivative.	4-Nitro- <i>m</i> -cresol, 	6-Nitro- <i>m</i> -cresol, 	2-Nitro- <i>m</i> -cresol, 
Free.	Yellow hexagonal plates from benzene. M. p. 56°; smell of <i>o</i> -nitrophenol; volatile in steam.	Colourless prisms from water. M. p. 129°; no smell; non-volatile in steam.	Fern-like rhombic groups of deep yellow needles from petrol. M. p. 41°; smell of <i>o</i> -nitrophenol; volatile in steam.
Sodium.	Bright red needles, sparingly soluble in cold water.	Yellow plates, sparingly soluble in cold water.	Crimson, extremely soluble in cold water.
Acetyl	Large, hexagonal tablets. M. p. 47°.	Tough masses of fine needles. M. p. 34°.	Long, thick needles. M. p. 59°.
Benzoyl	* Rectangular prisms. M. p. 77°.	* Fine needles. M. p. 74°.	Felted mass of extremely fine needles. M. p. 79°.
Methyl	† Rectangular prisms or plates. M. p. 62°. No smell.	† Fine needles. M. p. 53°. Characteristic odour.	Large, hexagonal plates. M. p. 54°. Smell of iodoform.

* Compare *Ber.*, 1898, **31**, 394, 398; 1902, **35**, 1259; 1909, **42**, 3100.

† Compare *Annalen*, 1904, **330**, 99.

In order to determine the orientation of the groups in these three nitro-compounds, the methyl derivative of each was oxidised to the corresponding nitromethoxybenzoic acid, the properties of which are known (compare Rieche, *Ber.*, 1889, **22**, 2352). The results of these experiments showed that the methyl derivatives of the 4- and of the 6-nitro-*m*-cresol gave the expected acids melting at 208° and 132°, respectively, and the supposed 2-nitro-*m*-cresol gave a nitromethoxybenzoic acid, melting at 250° with decomposition, which is in all probability identical with the acid $[\text{CO}_2\text{H} : \text{NO}_2 : \text{OMe} = 1 : 2 : 3]$, melting at 251° with decomposition, described by Rieche (*loc. cit.*).

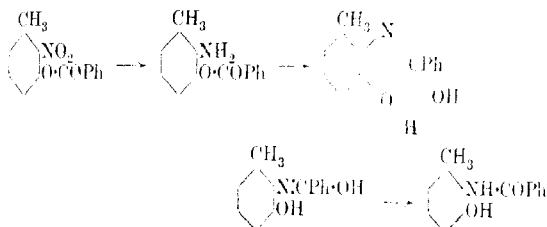
In order to determine conclusively the structure of the new nitro-*m*-cresol, the compound was transformed into 3-methoxycyphthalic acid by the following series of changes:



The final product melted at 159° and gave an anhydride melting at 87° , thus proving its identity with 3-methoxyphthalic acid (Jacobson, *Ber.*, 1883, **16**, 1965).

As oily by-products were always obtained in preparing the crystalline derivatives from the crude 2-nitro-*m*-cresol, the presence of an isomeric nitro-*m*-cresol was suspected. In order to clear up this matter, the oily residues from the preparation of the methyl derivative were oxidised to the corresponding nitromethoxybenzoic acids and from the product, which melted indefinitely at $215\text{--}245^{\circ}$, 4-nitro-*m*-methoxybenzoic acid, m. p. 208° , and 2-nitro-*m*-methoxybenzoic acid, m. p. 250° , were finally isolated. Therefore 4-nitro-*m*-cresol is the impurity in the crude 2-nitro-*m*-cresol prepared as described above.

The oily by-product from the benzoylation of crude 2-nitro-*m*-cresol was also examined. On reduction, this oil gave a mixture from which two compounds were finally obtained in the pure state; these compounds melted at 189° and 169° , respectively, and were identical with the derivatives prepared from pure 2- and 4-nitro-*m*-tolyl benzoates. It is very interesting to note that these products are benzoylated amines, whereas the original nitro-compounds are benzoylated phenols: the benzoyl group wanders from the oxygen to the nitrogen atom during the reduction:



The benzoyl group in *o*-nitrophenyl benzoate undergoes the same migration on reduction, possibly in the manner indicated above (Hübner, *Annalen*, 1881, **210**, 884). This view seems to be confirmed by the fact that in the case of 6-nitro-*m*-tolyl benzoate, where such ring formation is not to be expected, the normal reduction product, a base, is readily obtained (compare *J. Amer. Chem. Soc.*, 1919, **41**, 2068; 1922, **44**, 1792; 1923, **45**, 469).

EXPERIMENTAL.

Nitration of *m*-Cresol.

To a cold solution of *m*-cresol (21.6 c.c.) in fuming sulphuric acid (6–7% SO_3 ; 80 c.c.) a mixture of fuming sulphuric acid

(6–7% SO_3 ; 21.3 c.c.) and nitric acid (9.3 c.c. of d 1.5) was very gradually added. After twenty-four hours, the liquid was diluted with water (100 c.c.) and superheated steam passed through the heated solution. Below about 145° a little unchanged cresol distilled, but above this temperature up to 180° nitrocresol passed over, leaving a black tar from which no crystalline compound could be isolated. The distillate, which was a butter-like emulsion, was extracted with ether; the extract, on evaporation, gave a yellow oil, the weight of which was equal to that of the *m*-cresol taken.

2-Nitro-*m*-cresol.—As the crude nitration product did not crystallise readily, it was treated with acetic anhydride and a pure acetyl derivative isolated; the latter was then hydrolysed with alcoholic sodium hydroxide solution, the alcohol evaporated, and the dark-coloured oil which separated on the addition of acid distilled in steam. The volatile product solidified readily and separated from light petroleum in bright yellow, fern-like, rhombic groups of needles melting at 41° .

With the exception of light petroleum, 2-nitro-*m*-cresol is readily soluble in the ordinary organic solvents and its sodium salt forms a deep crimson solution in water (Found: C = 55.9; H = 4.8. $\text{C}_7\text{H}_7\text{O}_3\text{N}$ requires C = 54.9; H = 4.6 per cent.).

2-Nitro-*m*-tolyl Acetate.—This derivative was obtained by boiling the crude nitro-compound for two hours with an excess of acetic anhydride and fractionating the product under reduced pressure (15 mm.). The main fraction, collected from 160° to 180° , partly solidified, and, when freed from oil with the aid of porous earthenware, crystallised from alcohol in long, thick, colourless needles melting at 59° (Found: C = 55.5; H = 4.88. $\text{C}_9\text{H}_9\text{O}_4\text{N}$ requires C = 55.4; H = 4.61 per cent.).

4-Nitro-*m*-tolyl acetate, prepared in a similar manner from the 4-nitro-compound (Staedel, *loc. cit.*), crystallised from alcohol in large, hexagonal tablets melting at 48° .

6-Nitro-*m*-tolyl acetate, prepared from 6-nitro-*m*-cresol (Staedel, *loc. cit.*), crystallised from alcohol in tough, felted masses of fine needles melting at 34° .

These three esters are readily soluble in alcohol, benzene, acetone, and the usual organic solvents.

2-Nitro-*m*-tolyl Benzoate.—The crude benzoyl derivative, which was obtained by treating the above-described crude nitro-*m*-cresol with benzoyl chloride and alkali and then extracting with ether, crystallised readily and was freed from oily impurities by draining it on porous earthenware. It separated from alcohol in colourless, extremely fine needles melting at 79° and was sparingly soluble in alcohol or light petroleum, but easily soluble in benzene, acetone,

ethyl acetate, or chloroform (Found: C = 65.8; H = 4.67. $C_{11}H_{11}O_3N$ requires C = 65.4; H = 4.28 per cent.). The 4- and 6-nitro-*m*-tolyl benzoates (*Annalen*, 1904, 330, 99) were prepared in a similar manner and directly compared with the above benzoyl derivative.

2-Nitro-*m*-tolyl Methyl Ether.

The crude nitro-*m*-cresol described above, methylated with alkali and methyl sulphate, gave an emulsion when shaken with ether. The oily product was therefore separated by steam distillation and extracted. When distilled (15 mm.), it gave first a little *m*-tolyl methyl ether, then a mixture of *m*-tolyl methyl ether and 2-nitro-*m*-tolyl methyl ether (120–150°), and finally the nitrotolyl methyl ether alone (150–160°). The two later fractions partly solidified, and this product, when freed from oil, separated from alcohol in large, yellow, hexagonal plates melting at 54°. This ether has a pleasant, characteristic odour similar to that of iodoform, and is readily soluble in most of the ordinary solvents (Found: C = 57.8; H = 5.55. $C_8H_9O_3N$ requires C = 57.5; H = 5.39 per cent.).

For the purpose of direct comparison, 4- and 6-nitro-*m*-cresols were submitted to the above process of methylation, when compounds were obtained the properties of which corresponded well with those described by Foehner and Rigaud (*Ber.*, 1902, 35, 1259), by Reissert (*Ber.*, 1898, 31, 394), and by Khotinsky and Jacopson-Jacopmann (*loc. cit.*).

The above results showed that a new nitro-*m*-cresol had been prepared, probably the 2-nitro-derivative.

Oxidation of 2-Nitro-*m*-tolyl Methyl Ether.

2-Nitro-*m*-tolyl methyl ether was oxidised by boiling dilute permanganate; the product crystallised from 50 per cent. aqueous alcohol in well-defined needles melting at 250° with decomposition, and was evidently identical with the 2-nitro-3-methoxybenzoic acid prepared by Rieche (*loc. cit.*). It dissolved freely in acetone, but was very sparingly soluble in hot chloroform or water (Found: equivalent = 195.6. $C_8H_7O_5N$ requires equivalent = 197).

*Conversion of 2-Nitro-*m*-cresol into 3-Methoxyphthalic Acid.*
3-Methoxy-*o*-toluidine.—2-Nitro-*m*-tolyl methyl ether was reduced with iron and boiling dilute aqueous acetic acid, and the resulting base, liberated by excess of caustic soda, was distilled in steam and isolated by extraction with ether. 3-Methoxy-*o*-toluidine was thus obtained in almost theoretical quantity; it crystallised from water in colourless needles melting at 31° and was readily soluble in organic solvents, but was only sparingly soluble in cold water. The base, if finely powdered, rapidly discoloured in the air, but coloured

samples were readily purified by distillation (b. p. 124—126°/15 mm.). The odour of this compound is very pronounced and resembles that of α -naphthylamine to some extent.

The *benzoyl* derivative, prepared by the Schotten-Baumann method, crystallised from dilute alcohol in colourless needles melting at 137° and was readily soluble in the usual solvents (Found: C = 74.6; H = 6.4; N = 5.75. $C_{16}H_{13}O_2N$ requires C = 74.75; H = 6.23; N = 5.82 per cent.).

3-Methoxy-o-toluanitrile.—The base just described was diazotised and the solution added drop by drop to a well-stirred solution of sodium cupro-cyanide, heated at 80°. After distillation in steam, the product solidified and was crystallised from light petroleum. The nitrile was thus obtained in colourless needles melting at 64° and, with the exception of light petroleum, was readily soluble in organic crystallising media (Found: C = 73.3; H = 6.24. C_9H_9ON requires C = 73.5; H = 6.12 per cent.).

3-Methoxy-o-toluamide.—Some little difficulty was found in hydrolysing this nitrile, probably owing to the presence of the two ortho-substituents to the -CN group. The best method seemed to be the following.

The crude nitrile (10 grams) was boiled during sixty hours with alcohol (50 c.c.) and caustic soda (10 grams). The alcohol was then distilled off, water added to the residue, and the undissolved solid separated by filtration. It crystallised from hot water in colourless, twig-like needles melting at 157°, and was sparingly soluble in organic solvents. Yield = 10 grams (Found: C = 65.7; H = 6.96. $C_9H_{11}O_2N$ requires C = 65.5; H = 6.67 per cent.).

Many attempts were made to hydrolyse this amide to the corresponding acid by the usual methods, and one very interesting result was obtained. The amide was boiled during twenty-four hours with concentrated hydrochloric acid, when an oil was observed in the condenser. On distillation in steam, 80 per cent. of the amide was left in the flask unchanged, whilst a colourless oil passed over. This product boiled at 177° and was proved to be *m*-tolyl methyl ether by the fact that on oxidation with boiling dilute permanganate it gave *m*-methoxybenzoic acid, melting at 107°. As 3-methoxy-*o*-toluic acid (see below) does not lose carbon dioxide on boiling with concentrated hydrochloric acid, it seems likely that the amide group is directly displaced by hydrogen instead of undergoing the usual transformation. This curious change is being further investigated with a view to discover the course of the reaction.

3-Methoxy-o-toluic Acid.—This acid was finally obtained by stirring the amide with a solution of nitrous acid during many hours. The suspension was evaporated to dryness and the residue extracted

with warm ether. The extract, on evaporation, gave a mixture of acid and amide which was boiled with dilute ammonia. After cooling, most of the unchanged amide was separated by filtration. To remove the remaining small proportion of amide, the silver salt was precipitated from the neutral solution of the ammonium salt and then decomposed by hydrogen sulphide. The filtrate from the silver sulphide gave on evaporation a brown, crystalline residue, which was recrystallised twice from light petroleum. 3-Methoxy-*o*-toluic acid was thus obtained in colourless leaflets melting at 112°; it was readily soluble in alcohol or acetone, but insoluble in petroleum, benzene, or chloroform (Found: C = 65.25; H = 6.22; equivalent = 165.5, 165.7. $C_9H_{10}O_3$ requires C = 65.1; H = 6.03 per cent.; equivalent = 166).

The above acid, dissolved in dilute sodium carbonate, was treated with the theoretical amount of permanganate on a warm water-bath. When oxidation was complete, the filtered solution was evaporated to dryness and extracted with warm ether. The residue from the ethereal solution sublimed easily in colourless needles, m. p. 87°, of the anhydride of 3-methoxyphthalic acid.

On boiling this compound with water and allowing the solution to cool, prisms of 3-methoxyphthalic acid were obtained melting at 159°. Jacobson (*Ber.*, 1883, **16**, 1965) gives 87° and 160° as the melting points of the anhydride and the acid, respectively (Found: C = 55.1; H = 4.17; equivalent = 96.7. Calc., C = 55.15; H = 4.08 per cent.; equivalent = 98).

Examination of the Oily By-products.

A portion of the oily by-products from the preparation of 2-nitro-*m*-tolyl methyl ether (p. 1273) was fractionated under 15 mm. pressure; the first fraction (90—100°) consisted of *m*-tolyl methyl ether, which boiled under the ordinary pressure at 177° and gave *m*-methoxybenzoic acid (m. p. 107°) on oxidation with permanganate. The fraction of higher boiling point (150—160°) deposited a small quantity of the crystalline methyl derivative (m. p. 54°), which was separated. The oily methyl derivative was then oxidised with boiling dilute permanganate solution and the filtered solution acidified. The crude crystalline product melted from 215° to 245°; when extracted with hot chloroform, a part dissolved and was obtained by recrystallising from water in fine, silky needles melting at 208°. This compound was 4-nitro-*m*-methoxybenzoic acid, identical with the acid prepared from 4-nitro-*m*-tolyl methyl ether. The acid, not extracted by boiling chloroform, crystallised from 50 per cent. aqueous alcohol in well-defined needles melting at 250° with decomposition and was proved to be identical with

2-nitro-*m*-methoxybenzoic acid, obtained by the oxidation of 2-nitro-*m*-tolyl methyl ether (p. 1273).

To confirm the above results, which showed that the only impurity in the crude nitration product was 4-nitro-*m*-cresol, the oily by-products from the crystalline benzoyl derivative (p. 1272) were submitted to reduction in order to convert them into substances of high melting points which could then be more fully examined. For this purpose the oil was reduced with iron in boiling dilute acetic acid, and the liquid neutralised with sodium hydrogen carbonate (which gave a less flocculent precipitate than sodium carbonate or hydroxide). The iron residue was removed and the dried powder extracted with warm ether. The extract, when concentrated, gave a crystalline deposit of very indefinite melting point (150–185°); when this product was recrystallised from a mixture of acetone (1 volume) and light petroleum (5 volumes), it gave long, spear-like needles and a crust of small, rhombic plates. The needles were easily picked out and when recrystallised from a little ethyl acetate melted sharply at 169°. The plates were again crystallised from light petroleum and acetone, and now they melted at 189°. The two compounds were identical with the derivatives prepared as described later from 4-nitro-*m*-tolyl benzoate and 2-nitro-*m*-tolyl benzoate, respectively.

N-Benzoyl-2-amino-m-cresol.—Pure crystalline 2-nitro-*m*-tolyl benzoate (p. 1272) was treated with iron and dilute acetic acid as described above; the sole product in this case was the compound which crystallised in rhombic plates melting at 189°. This benzoyl derivative was readily soluble in dilute alkali, usually giving a pale green solution which, with a diazo-solution, readily yielded a yellow azo-compound; with more concentrated alkali, the sodium salt was precipitated in very fine needles.

With the exception of acetone, alcohol, and ethyl acetate, this phenol is sparingly soluble in organic solvents and may be crystallised from benzene or a mixture of acetone and light petroleum (Found: C = 73.9; H = 5.79; N = 6.05. $C_{14}H_{13}O_2N$ requires C = 74.0; H = 5.73; N = 6.17 per cent.).

N-Benzoyl-4-amino-m-cresol.—4-Nitro-*m*-tolyl benzoate (p. 1273) was reduced under the conditions described above. The product crystallised in spear-like needles from a mixture of acetone and light petroleum and melted at 169°. The sodium salt, azo-derivative, and solubilities are very similar to those described for *N*-benzoyl-2-amino-*m*-cresol.

6-Amino-m-tolyl Benzoate.—6-Nitro-*m*-tolyl benzoate (p. 1273) was reduced with iron and acetic acid in the manner already described and the product extracted with ether from the precipitated

hydroxides of iron. The extract had a bright red colour and gave on evaporation a crystalline residue, which was recrystallised from light petroleum with the addition of animal charcoal. The crystals thus obtained were colourless needles melting at 92° . This base was soluble in ordinary solvents except light petroleum and could be obtained in large, hexagonal tablets by the spontaneous evaporation of its solution in acetone. On exposure to the air, a slight pink colour usually appeared, which deepened continuously, probably owing to atmospheric oxidation, and could only be removed by repeated crystallisation or by distillation in a vacuum (b. p. $220^{\circ}/12$ mm.) (Found: C = 74.0; H = 5.8; N = 6.37. $C_{14}H_{13}O_2N$ requires C = 74.0; H = 5.73; N = 6.17 per cent.).

Its *hydrochloride* was prepared by dissolving the base in dry ether and passing dry hydrogen chloride, when a white precipitate rapidly formed. On filtering and drying the salt, a colourless powder was obtained which was readily soluble in water (Found: Cl = 13.39. $C_{14}H_{13}O_2N.HCl$ requires Cl = 13.48 per cent.).

In conclusion, the author wishes to express his gratitude to the Department of Scientific and Industrial Research for a maintenance grant which allowed him to carry out the above work, and to Professor Kipping, F.R.S., for many helpful suggestions and kindly criticisms.

UNIVERSITY COLLEGE,
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[Received, February 20th, 1923.]

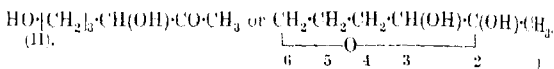
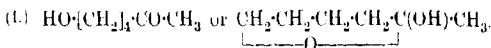
CXLVIII.—The Structure of Sucrose.

By MAX BERGMANN.

THE formula of sucrose that has been almost generally accepted in recent years displays an ethylene-oxide ring in the fructose portion of the molecule, this structure having been assigned by Haworth and Law on the ground that octamethyl sucrose, when hydrolysed, yields a tetramethyl fructose which reduces permanganate as does ethylene oxide. Later, Haworth oxidised this tetramethyl fructose with nitric acid and obtained the bimolecular semilactide of trimethylated tetrahydroxyvaleric acid, the free hydroxyl group of which was supposed to be in the α -position to the carboxyl. He therefore attributed the ethylene-oxide formula to sucrose and rejected other formulæ, such as the one with a 2:6-oxide ring.

I have recently studied a number of glucoside-like *cycloacetals* of hydroxy-aldehydes and ketones, the oxide ring of which does

not show the 1:4-structure. Having doubted for a long time the ethylene-oxidic structure of sucrose, I was especially interested in the study of δ -acetyl-*n*-butyl alcohol (I) and δ -hydroxy- δ -acetyl-*n*-butyl alcohol (II), in both of which the carbonyl group is in the same position as it is in fructose. It was no accident that the work was started with the methylcelloacetal of acetylbutyl alcohol, that is, with a substance which can have no other oxide ring than a 2:6-ring (Bergmann and Mickleley, *Ber.*, 1921, **54**, [B], 2157; 1922, **55**, [B], 1390).



The result of these studies as far as it concerns the structure of sucrose was published in the following words, with particular reference to the views of Haworth:

„Die Eigenschaften des neuen Acetobutylalkohol-halbacetals zeigen nunmehr, dass die am Rohrzucker festgestellte leichte Spaltbarkeit keineswegs ausschliesslich mit einem äthylenoxydartigen Ringsystem zusammenzuhängen braucht, sondern auch bei Ketosiden anderer Struktur auftritt. Dazu kommt noch, dass sowohl der Acetobutylalkohol wie sein Halbacetal Permanganat leicht entfärben, auch in neutraler Lösung. Für den Rohrzucker ergibt sich hieraus, dass seine Formel in Bezug auf die Struktur des Fruktoserestes erneut unsicher geworden ist und auf anderer Grundlage, als es bisher versucht wurde, neu bestimmt werden muss. Wir führen selbst dahingehende Versuche aus.“

We stated that the structure of raffinose, inulin, levulosan, and similar substances which were hitherto supposed to be of the ethylene-oxide type in the fructose portion of the molecule must also be redetermined.

In conjunction with Dr. Erich Correns, I began the study of sucrose a year ago. We obtained from methylated sucrose a compound, $\text{C}_6\text{H}_6\text{O}(\text{O}\cdot\text{CH}_3)_4$, which is derived from the fructose portion of sucrose and contains four methoxyl groups. This compound is unsaturated, and the dark red coloration developed with fuming hydrochloric acid proves that the oxide ring is present as a 5- or 6-ring. We were unable to proceed with this work for many months, and therefore could not give accurate and complete results.

I note with pleasure that Prof. Haworth (this vol., pp. 294, 301) agrees with me in doubting the correctness of the ethylene-oxidic structure of sucrose, after having succeeded, together with

Linnel, in converting the tetramethyl fructose derived from methylated sucrose into trimethoxyglutaric acid, the three methyl groups of which must have been united to the carbon atoms 3, 4, and 5 in the fructose portion of the methylated sugar. This means that an ethylene-oxide ring joining the atoms 2 and 3 cannot exist.

As our former deductions concerning the structure of sucrose may well have remained unknown to many fellow-workers—Prof. Haworth and Mr. Linnel apparently had no knowledge of them—it may be fitting to publish this brief notice.

KAISER WILHELM INSTITUT FÜR LEDERFORSCHUNG,
DRESDEN.

[Received, April 4th, 1923.]

CXLIX.—*The Action of Thiosulphates on Cupric Salts.*

By HENRY BASSETT and REGINALD GRAHAM DURRANT.

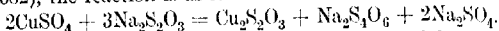
THE following investigation arose out of an observation of the late Henry Bassett, senior, that the filtrate from cuprous sulphide, precipitated by adding sodium thiosulphate to a hot acid solution of a cupric salt, contained a considerable quantity of pentathionic acid.

A considerable amount of work has been done on the interaction of sodium thiosulphate and metallic salts, especially by Vortmann, who (*Monatsh.*, 1886, 7, 418) proposed to use this thiosulphate instead of hydrogen sulphide as a laboratory reagent, since copper, mercuric, and bismuth salts together with the chlorides of antimony, arsenic, and tin are converted into sulphides when warmed with excess of thiosulphate in acid solution.

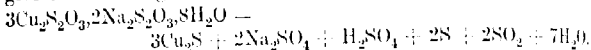
The present communication is concerned with copper only. The reactions involved in this case are of particular interest, because they furnish an excellent method for precipitating copper quantitatively as cuprous sulphide and of separating it from cadmium and zinc and from other metals of analytical group IV. As a rule, a more perfect separation is obtainable than with hydrogen sulphide. The method is described in several text-books (Classen, "Ausgewählte Methoden der Analytischen Chemie," 1901, I, 73; Beringer, "Text-book of Assaying," 10th ed., 1906, p. 183; Fresenius, "Quantitative Analysis," 7th English ed., 1876, p. 459, where early references to the method are given).

The reduction of copper to the cuprous condition is accompanied by oxidation of thiosulphate to tetrathionate. This was shown by Rammelsberg (*Pogg. Ann.*, 1842, 56, 321) in the case of potassium thiosulphate, and by Zettnow (*Z. anal. Chem.*, 1867, 6, 438) in the

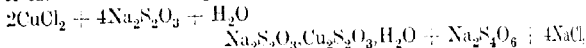
case of the sodium salt. According to von Renesse (*Ber.*, 1877, **10**, 1682), the reaction is as follows:



Vortmann (*Monatsh.*, 1888, **9**, 165) stated that sulphuric acid is not produced as had been asserted independently by Sievert (*Pogg. Ann.*, 1842, **56**, 321) and Kessel (*Ber.*, 1877, **10**, 1677, 2000; 1878, **11**, 1581). None of these workers appears to have made quantitative determinations of the tetrathionate which is produced. C. and I. Bhaduri (*Z. anorg. Chem.*, 1898, **17**, 1) refer to Vortmann (*loc. cit.*, 1888), who obtained a bright yellow, crystalline salt to which he assigned the formula $3\text{Cu}_2\text{S}_2\text{O}_3 \cdot 2\text{Na}_2\text{S}_2\text{O}_3 \cdot 8\text{H}_2\text{O}$, and they give the following reaction as occurring when this salt is heated:



We have arrived at this reaction from our bright yellow salt, which contains 6 instead of 8 molecules of water, and have found that the relative formula-weights of cuprous sulphide, sulphur, and sulphuric acid are exactly as 3 : 2 : 1. We have also made a quantitative determination of the amount of tetrathionate produced during the formation of the white salt, $\text{Na}_2\text{S}_2\text{O}_3 \cdot \text{Cu}_2\text{S}_2\text{O}_3 \cdot \text{H}_2\text{O}$, and find that it tallies with that required for the reaction

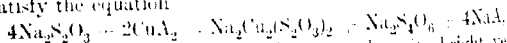


in which no sulphuric acid is produced.

Any sulphuric acid which may have been found by Sievert and Kessel was probably due to partial decomposition of one of the double salts. Von Renesse's reaction would suggest that cuprous thiosulphate is actually produced, but our work has shown that double salts are immediately formed and that cuprous thiosulphate itself, if it exists at all, is exceedingly unstable.

Investigation of the sodium cuprous thiosulphates formed in the reaction has thrown some interesting sidelights on other sodium cuprous double salts.

When *N*-solutions of cupric chloride, sulphate, or nitrate are mixed with *N*- or 2*N*-solutions of sodium thiosulphate in proportions to satisfy the equation



a yellow solution is produced which soon deposits bright yellow, prismatic crystals at the ordinary temperature. This yellow salt in the case of copper nitrate corresponds exactly with the formula $2\text{Na}_2\text{S}_2\text{O}_3 \cdot 3\text{Cu}_2\text{S}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$. When prepared from cupric chloride solution, the yellow double thiosulphate first formed soon changes into a white salt, the change being complete in a few hours. This white salt is crystalline (prisms) and perfectly homogeneous under

the microscope, but always contains a considerable quantity of chloride. The analytical figures agree perfectly with a compound $\text{Na}_2\text{Cu}_2(\text{S}_2\text{O}_3)_2 \cdot \text{H}_2\text{O}$ containing varying amounts of isomorphous $\text{Na}_2\text{Cu}_2\text{Cl}_4 \cdot \text{H}_2\text{O}$ in solid solution. This particular complex cuprous chloride does not appear to have been prepared, although a number of others have been (see Abegg's "Handbuch," 1908, II, i, 550). The amount of chloride present in these preparations is always greater than the amount of sulphate which in similar circumstances appears in the yellow salt obtained from copper sulphate. It is less in presence of free hydrochloric acid than in its absence. These are both results which might be expected. It is well known that solid cuprous sulphate cannot exist in presence of water, as it breaks up into cupric sulphate and metallic copper. As the "neutral part" of a complex ion, it is more stable and the opportunity of entering into solid solution in the double thiosulphate would still further protect it. No double cuprous sulphates appear to have been actually prepared, but it seems clear that they are capable of existence under favourable conditions. The existence of complex cuprous sulphate-ions in aqueous solution has been proved by Abel (*Z. anorg. Chem.*, 1901, **26**, 361).

Double nitrates practically only exist when one of the constituent metals is trivalent: hence the freedom from contaminating nitrate in the double thiosulphate prepared from cupric nitrate is not surprising. The tetrathionate formed in the reaction might have had some tendency to form similar solid solutions to the above, but no evidence for this has been found, although specially looked for.

The formation of solid solutions of sodium cuprous chloride in sodium cuprous thiosulphate is of interest in connexion with the compounds $\text{CuX} \cdot \text{NH}_4\text{X} \cdot 4(\text{NH}_4)_2\text{S}_2\text{O}_3$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{CN}, \text{S}$) obtained by Rosenheim and Steinhäuser (*Z. anorg. Chem.*, 1900, **25**, 103) by the action of saturated solutions of ammonium thiosulphate on cuprous chloride, etc. (see also Canneri and Lucchini, *Gazzetta*, 1922, **52**, ii, 261, for similar sodium compounds).

The following list of double cuprous thio-sulphates, with references, is given by Vortmann (*loc. cit.*, 1888):

(1) Bright yellow salt, first obtained by von Hauer (*Sitzungsber. Akad. Wiss. Wien*, 1854, [ii], **13**, 443) and erroneously considered to be $\text{Cu}_2\text{S}_2\text{O}_3 \cdot 2\text{H}_2\text{SO}_3$. This undoubtedly is the same salt to which Vortmann assigns the formula $2\text{Na}_2\text{S}_2\text{O}_3 \cdot 3\text{Cu}_2\text{S}_2\text{O}_3 \cdot 8\text{H}_2\text{O}$. (2) A white salt obtained by Russel (*Chem. Ztg.*, 1894, **9**, 233) from copper chloride—formula $\text{Na}_2\text{S}_2\text{O}_3 \cdot \text{Cu}_2\text{S}_2\text{O}_3 \cdot \text{H}_2\text{O}$. He does not give details of preparation or analysis. (3) A pale greenish-yellow salt consisting of very small prisms, obtained by Vort-

mann from copper sulphate—formula $\text{Na}_2\text{S}_2\text{O}_3 \cdot \text{Cu}_2\text{S}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$, (4) $2\text{Na}_2\text{S}_2\text{O}_3 \cdot \text{Cu}_2\text{S}_2\text{O}_3 \cdot 4\text{H}_2\text{O}$, (5) $2\text{Na}_2\text{S}_2\text{O}_3 \cdot \text{Cu}_2\text{S}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$, (6) $3\text{Na}_2\text{S}_2\text{O}_3 \cdot \text{Cu}_2\text{S}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$, (7) $4\text{Na}_2\text{S}_2\text{O}_3 \cdot \text{Cu}_2\text{S}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$. Apparently Lenz (*Annalen*, 1841, 40, 99), Rammelsberg, Russel, Jochun (*Inaug. Diss. Berlin*, 1885), and Vortmann agree as to the existence of the last four. C. and I. Bhaduri (*loc. cit.*) quote all these and three more double salts.

We have confirmed the existence of the first three salts. We find (1) contains only 6 molecules of water, (2) is always contaminated with chloride, whilst (3) agrees in every particular with Vortmann's description and analysis.

We have reason to believe that several of the other salts are merely mixtures, and are hoping soon to complete our study of the system $\text{Na}_2\text{S}_2\text{O}_3$ — $\text{Cu}_2\text{S}_2\text{O}_3$ — H_2O .

The mother-liquors from the preparations of double thiosulphates always contain excess of thiosulphate in addition to sodium tetrathionate and nitrate (chloride or sulphate), and some copper is still present in solution. This was the case in all experiments made with varying proportions and concentrations of the reactants. Some atmospheric oxidation of cuprous copper appears to occur during the reaction, but as long as sodium thiosulphate is in excess the cupric copper will be again reduced.

In all experiments in which acid was used there was strong evidence of the formation of pentathionic acid. This was traced to the action of mineral acid liberating sulphur from sodium thiosulphate. Some of this sulphur unites with the tetrathionate present. Pentathionic acid is very stable in presence of hydrogen-ions.

We are endeavouring to prepare double pentathionates starting with concentrated solutions of cupric nitrate and ammonium thiosulphate. When these solutions are mixed, a light yellow liquor is formed from which a bright yellow salt separates. This very rapidly changes to a white, crystalline salt having the formula $3(\text{NH}_4)_2\text{S}_2\text{O}_3 \cdot 2\text{Cu}_2\text{S}_2\text{O}_3 \cdot \text{H}_2\text{O}$.

All the above double thiosulphates are decomposed by mineral acids, slowly in the cold, more quickly on warming, with formation of cuprous sulphide, sulphur, sulphurous and sulphuric acids. When using thiosulphate for precipitating copper quantitatively as cuprous sulphide, the sodium thiosulphate is usually added to the hot acid solution containing copper, and the formation and the decomposition of the sodium cuprous thiosulphate occur practically simultaneously. The filtrate from the precipitated cuprous sulphide and sulphur contains large amounts of polythionates, mainly pentathionate, but possibly some unaltered tetra-

thionate as well. If other metals are to be estimated, it is frequently advisable first to remove these polythionates by concentrating the filtrate, adding strong nitric acid, and filtering off the liberated sulphur after digesting the mixture for some time so as to render the sulphur capable of filtration. If this is not done, sulphur will be liberated from the pentathionate on addition of ammonia, and this may cause trouble.

Those who have had much experience in this method of separating copper will have noticed that a trace of copper is frequently left in solution, although its amount is usually far too minute to be of any consequence. We have found that this occurs most readily from chloride solutions, less readily from sulphate, and not at all with nitric acid solutions, provided too much acid is not present. The explanation is to be sought in the tendency to form complex cuprous chlorides or sulphates. These cannot decompose to give cuprous sulphide; only the complex cuprous thiosulphate can do that. At any moment there will be some sort of equilibrium in the solution between the complex cuprous thiosulphates and chloride or sulphate. As the former decomposes and more sodium thiosulphate is added, the amount of complex cuprous chloride or sulphate remaining in the solution will rapidly diminish, but a trace will probably remain. Comparative experiments have shown that the most suitable acid to use in this method of estimating copper is sulphuric acid—because nitric acid, if above half-normal concentration, causes slight oxidation of copper when the solution is at the boiling point, whereas sulphuric acid, if used in considerable excess and heated with any copper salt before adding the thiosulphate, prevents the formation even of the complex cuprous chlorides, and no trace of copper appears in the filtrate from the black precipitate. If hydrochloric acid is used instead of sulphuric, it may be exceedingly difficult to precipitate all the copper.

EXPERIMENTAL.

Action of Sodium Thiosulphate on Cupric Chloride in Presence of Hydrochloric Acid.

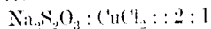
Normal solutions of the above were mixed together in the volume proportions 2:1:1. A white, crystalline salt appeared after a few hours and after a few days the salt was drained through a Büchner funnel, washed with a little water, then with alcohol, and air-dried (Found: Na = 11.35; Cu = 31.25; S = 27.30. 90% of $\text{Na}_2\text{Cu}_2(\text{S}_2\text{O}_3)_2 \cdot \text{H}_2\text{O} + 10\%$ of $\text{Na}_2\text{Cu}_2\text{Cl}_4 \cdot \text{H}_2\text{O}$ requires Na = 11.35; Cu = 31.35; S = 27.75 per cent.). Chlorine and water, the presence of which was proved qualitatively, were not estimated.

The prismatic crystals, examined under the microscope, were

seen to be colourless and homogeneous. In these and in subsequent experiments copper was precipitated as cuprous sulphide by warming with sulphuric acid and was weighed either as such or after ignition to oxide; the sulphur was estimated as barium sulphate, thiosulphate by iodine titration, and sodium as sulphate in a platinum dish. In every case, except with the double thio-sulphates prepared from cupric nitrate, it was found that a small amount of copper remained with the fused sodium sulphate. This was estimated and allowed for.

Action of Sodium Thiosulphate on Cupric Chloride in Absence of Acid.

Normal solutions were mixed in the volume proportions



and left at room temperature. A bright yellow precipitate soon separated, but this disappeared within two days, giving place to white crystals. After five days, the white deposit became slightly blue on the surface owing to atmospheric oxidation. This small blue portion having been removed, the remainder was washed with water and with alcohol and dried in the air (Found: Na = 11.55; Cu = 31.89; $\text{S}_2\text{O}_3 = 44.66$; Cl = 7.42; H_2O (by diff.) = 4.48, 82.6% of $\text{Na}_2\text{Cu}_2(\text{S}_2\text{O}_3)_2 \cdot \text{H}_2\text{O} = 17.4\%$ of $\text{Na}_2\text{Cu}_2\text{Cl}_2 \cdot \text{H}_2\text{O}$ requires Na = 11.56; Cu = 31.90; $\text{S}_2\text{O}_3 = 44.58$; Cl = 7.42; $\text{H}_2\text{O} = 4.52$ per cent.).

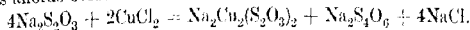
Owing to the fact that the salt is decomposed at temperatures below 100° , a direct estimation of the water was not made. The salt, when heated in a hard glass tube, after discharging water, sulphur dioxide, and excess of sulphur as vapour, left a residue (75.28 per cent.) consisting chiefly of sodium sulphate and cuprous sulphide but containing also sodium chloride. If the whole of the copper from $\text{Na}_2\text{Cu}_2\text{Cl}_2 \cdot \text{H}_2\text{O}$ is converted into cuprous sulphide, the residue by theory should be 74.33 per cent.; if none of it is so converted, the residue should be 76.39 per cent.; if half of it is converted, the residue should be 75.36 per cent.

The fact, previously noted, that copper is found in the fused sodium sulphate (after treatment with acid and precipitation of cuprous sulphide) is explained by supposing that this double chloride escapes complete conversion into cuprous sulphide.

Examination of the Filtrate from the White Salt. Fifty c.c. of *N*-cupric chloride were left for six days with 100 c.c. of *N*-sodium thiosulphate, and the whole of the filtrate was then collected (136 c.c. without wash water). The copper in the precipitate, in the wash water, and in aliquot portions of the filtrate was estimated, the results agreeing well with the known weight in the original

solution. Five estimations were made each with 10 c.c. of the filtrate, giving sulphur (as thiosulphate) 0.0620, sulphur (total) 0.2054, copper 0.0488, chlorine 0.1077, and sodium 0.1477 gram.

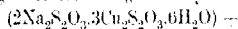
Assuming chlorine to be present as cuprous chloride and sodium chloride, and sodium as sodium chloride, sodium thiosulphate, and sodium tetrathionate, these figures show that the amounts of sodium and of sulphur in excess of those required to produce the cuprous chloride, sodium chloride, and sodium thiosulphate are 0.0511 gram and 0.1434 gram, respectively. The theoretical ratio for sodium tetrathionate is 0.0511 of sodium to 0.1422 of sulphur. This affords evidence for the fundamental reaction:



Further evidence was obtained by preparing the salt $\text{Na}_2\text{S}_4\text{O}_6 \cdot 2\text{H}_2\text{O}$ and comparing its properties with those of filtrates from double sodium copper thiosulphate precipitates.

The actual amount of sodium tetrathionate produced from a mixture of 50 c.c. of *N*-cupric chloride and 50 c.c. of 2*N*-sodium thiosulphate was estimated by Kurtcnacker and Fritsch's method (*Z. anorg. Chem.*, 1921, **117**, 292), using standard potassium cyanide, whereby tetrathionate is reconverted into thiosulphate. The results confirmed our suspicion that oxidation by air and subsequent reduction of the copper by thiosulphate take place, since the ratio of tetrathionate to copper was found to be higher than would have been the case if such alternating action had not occurred. In the examination of the above filtrate it was proved that one-quarter of the copper originally taken had been subjected to this alternating action, since the total copper corresponded to 1.6 as compared with 2 grams of tetrathionate sulphur found.

Examination of the Temporary Yellow Precipitate.—This examination was made after establishing the formula of the permanent yellow precipitates formed when copper sulphate and copper nitrate are used. The precipitate formed by mixing 50 c.c. of *N*-cupric chloride with 50 c.c. of 2*N*-sodium thiosulphate was collected after standing for five hours, drained with suction, washed with water and with alcohol, and air-dried as in all other similar preparations [Found: Cu = 31.74; S_2O_3 = 47.23; Cl = 2.26; residue on heating = 69.19. 70% of the yellow salt



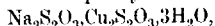
30% of the white salt (analysis given above; 17.4% double chloride) requires Cu = 32.84; S_2O_3 = 47.72; Cl = 2.23; residue after heating = 69.27 per cent.].

Portions of this precipitate, examined under the microscope, were seen to consist of a mixture of yellow and white crystals.

It is evident that the change from the yellow to the white salt

X X*

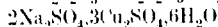
begins to take place at an early stage, although the yellow colour requires about two days to disappear completely. Earlier attempts to prepare white salts when using copper sulphate and copper nitrate were unsuccessful, but if 2*N*-copper nitrate is mixed with 4*N*-thiosulphate, Vortmann's pale yellow salt,



will be produced at room temperature.

Action of Sodium Thiosulphate on Copper Sulphate.

One hundred c.c. of *N*-sodium thiosulphate, mixed with 50 c.c. of *N*-copper sulphate, gradually deposited yellow crystals for eight days. The yield was 53 per cent., that is, 47 per cent. of the copper remained in the filtrate—and the ratio of thiosulphate in this filtrate to that from the white salt was 3:2. The air-dried yellow crystals were seen under the microscope to be perfectly homogeneous [Found: Na = 8.20; Cu = 33.49; S (as S_2O_3) = 26.58; S (as SO_4) = 0.66; S (total) = 27.24; residue after heating = 67.22. 93% of $2\text{Na}_2\text{S}_2\text{O}_3 \cdot 3\text{Cu}_2\text{S}_2\text{O}_3 \cdot 6\text{H}_2\text{O} + 7\%$ of



requires Na = 8.13; Cu = 33.71; S (total) = 27.16; residue after heating = 67.02 per cent.].

Action of Sodium Thiosulphate on Copper Nitrate.

One hundred c.c. of *N*-sodium thiosulphate, mixed with 50 c.c. of *N*-copper nitrate, deposited yellow crystals as in the last case, but here no nitrate could be detected in the yellow salt either by bicine or by other tests (Found: Na = 8.00; Cu = 33.28; S = 27.86; residue after heating = 67.41. $2\text{Na}_2\text{S}_2\text{O}_3 \cdot 3\text{Cu}_2\text{S}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$ requires Na = 8.06; Cu = 33.39; S = 28.04; residue after heating = 67.70 per cent.).

These results correspond with the pure salt. The residue after heating strongly consists entirely of cuprous sulphide and sodium sulphate. Larger quantities of this salt were prepared for subsequent experiments.

Properties of Disodium Tricuprous Thiosulphate.—This salt crystallises in bright yellow needles, those deposited during the early stages of the preparation being larger than those forming later on. If left in presence of the mother-liquor, the deposit will remain bright yellow for several weeks. The air-dried salt, if perfectly free from traces of tetrathionate, appears to be quite permanent, but if the crystals are not well washed (about 200 c.c. of water for a 40-gram yield), the salt will slowly decompose and eventually become quite black. When the salt was strongly heated in absence of air, the decomposition was shown to agree

with the reaction $3\text{Cu}_2\text{S}_2\text{O}_3 \cdot 2\text{Na}_2\text{S}_2\text{O}_3 \cdot 6\text{H}_2\text{O} = 3\text{Cu}_2\text{S} + 2\text{Na}_2\text{SO}_4 + \text{H}_2\text{SO}_4 + 2\text{SO}_2 + 2\text{S} + 5\text{H}_2\text{O}$. C. and I. Bhaduri (*loc. cit.*) arrived at the same reaction, assuming 8 instead of 6 molecules of water to be present.

The solubility of the salt in water at 10° appears to be 3 parts in 1000. After some time, a white cloud separates (possibly cuprous thiosulphate is formed and sodium thiosulphate dissolved). After twelve hours at 11° , the white suspension begins to hydrolyse— $\text{Cu}_2\text{S}_2\text{O}_3 + \text{H}_2\text{O} \rightarrow \text{Cu}_2\text{S} + \text{H}_2\text{SO}_4$ —after forty-eight hours, the hydrolysis has proceeded to the extent of 52 per cent. When the temperature is raised to 80° , this brown mixture becomes black and the extent of hydrolysis reaches 75 per cent., whilst after boiling for ten minutes it reaches 95 per cent.

The action of acids and of sodium thiosulphate—separately and together—on the salt has been studied with the view of finding a method which completely removes copper as cuprous sulphide from solution. From these experiments, it appears that the complete separation cannot be effected in presence of hydrochloric acid, but that it can be effected by excess of sodium thiosulphate in presence of nitric acid, provided the latter is not highly concentrated. The desired result can also be attained in sulphuric acid solution if sufficient acid be present to prevent the formation of complex double chloride or (less readily formed) double sulphate.

The Action of Ammonium Thiosulphate on Copper Nitrate.

On mixing 5*N*-ammonium thiosulphate and 2.5*N*-cupric nitrate in equal volumes, a bright yellow liquid was immediately produced, but no deposit was obtained after twenty hours' standing. Solutions of the preceding strength were concentrated and cooled separately, and then mixed together; after a short time, solidification occurred quite suddenly. The purple-grey, crystalline solid obtained was proved to contain traces of products of decomposition.

To another portion of the bright yellow liquid above mentioned an equal volume of alcohol was added. This immediately produced a bright yellow, crystalline solid, which became white in less than two minutes: it was separated, washed, and air-dried. (The wash-water was bright yellow and on the addition of alcohol again deposited white particles.) When dry, the white product assumed a pale buff colour (Found: $\text{NH}_4 = 11.54$; $\text{Cu} = 27.25$ (as Cu_2S), 27.09 (as CuO); $\text{S}_2\text{O}_3 = 58.34$, 58.34; residue after heating = 34.12. $3(\text{NH}_4)_2\text{S}_2\text{O}_3 \cdot 2\text{Cu}_2\text{S}_2\text{O}_3 \cdot \text{H}_2\text{O}$ requires $\text{NH}_4 = 11.49$; $\text{Cu} = 27.02$; $\text{S}_2\text{O}_3 = 59.57$; residue on heating = 33.83 per cent.].

These figures indicate triammonium dicuprous thiosulphate. The proportions in which the solutions were mixed were, as in all

$\text{XX}^{\frac{2}{2}}$

previous cases here cited, such as to favour the production of a double salt in *equimolecular* ratio. This salt appears to resemble the former white salt in crystallising with 1 molecule of water. The residue after strongly heating is pure cuprous sulphide. The filtrate from the separated salt contains ammonium tetrathionate.

Formation of Pentathionic Acid.

When copper chloride, sulphate or nitrate, is treated with excess of sodium thiosulphate in presence of any mineral acid, there is evidence to show that pentathionic acid is produced and remains in solution after cuprous sulphide and excess of sulphur have been thrown out by boiling. This must be due to interaction between sodium tetrathionate, sodium thiosulphate, and the mineral acid: $\text{Na}_2\text{S}_4\text{O}_6 + \text{Na}_2\text{S}_2\text{O}_3 + 4\text{HA}' \rightarrow \text{H}_2\text{S}_5\text{O}_6 + 4\text{NaA}' + \text{H}_2\text{O} + 8\text{O}_2$. The tests applied, which were those tabulated by Tamakatsu and Smith (T., 1880, **37**, 608) and by Debus (T., 1888, **53**, 297), gave positive results with the solutions here considered and also with mixtures prepared by adding sodium thiosulphate and acids to sodium tetrathionate, prepared from sodium thiosulphate and iodine (von Klebukow, *Ber.*, 1885, **18**, 1871).

Tests which Differentiate Pentathionic Acid from Colloidal Sulphur.—It is well known that certain chemists have been sceptical as to the existence of pentathionic acid. The literature up to 1887 was summarised by Debus (*loc. cit.*) and since then further papers have appeared from Berthelot, Spring, Hertlein, Lang and Carson, Valetton, Casolari, Maclaurin, W. Fell, and recently a longer paper by Riesefeld and G. W. Fell (*Z. anorg. Chem.*, 1921, **119**, 252). Among thirty authors, four only are sceptical, namely, Spring, Curtius, Pfeiffer, and Valetton. Valetton (*Chem. Weekblad*, 1907, **4**, 553) states that colloidal sulphur gives all the tests usually ascribed to pentathionates. We have confirmed this statement in so far as the following tests are concerned, which may be termed the "positive" tests of Debus:

1. Ammoniacal silver nitrate: immediate darkening (due to Ag_2S).
2. Caustic potash: immediate deposition of sulphur.
3. Ammonia alone: less rapid deposition of sulphur.
4. Ammonia containing H_2S : immediate deposition of sulphur.
5. Mercuric cyanide in aqueous ammonia: black precipitate forming slowly in the cold, rapidly on warming.

All these tests were equally successful with pentathionic acid (in presence of a trace of hydrochloric acid) and with colloidal sulphur prepared according to Svedberg (*Z. Chem. Ind. Kolloide*, 1900,

4, 49) (a concentrated solution of sodium thiosulphate is slowly added to concentrated sulphuric acid, the temperature being kept below 25° , and the precipitated sulphur is repeatedly centrifuged, separated, dissolved in water, reprecipitated by sodium chloride, and finally dissolved in pure water).

Among the "negative" tests given by Debus are: pentathionic acid gives no precipitate with HCl , CuCl_2 , FeCl_3 , CuAc_2 , CuSO_4 , or $\text{Co(NO}_3)_2$. We found this to be the case, but each of the above reagents gave an immediate precipitate of sulphur when added to the colloidal solution. Comparative experiments were also made with a number of other salts. The most delicate was that with didymium chloride; the merest trace of the tervalent cation precipitated sulphur from the colloidal solution, but a considerable amount failed to have any effect on pentathionic acid. Pentathionic acid, therefore, is unaffected by electrolytes provided the solution is not rendered alkaline. In this respect, it differs from colloidal sulphur. Another way to differentiate them is to boil each for a short time with hydrochloric acid and then apply Debus's "positive" tests involving alkali. It will be found that pentathionic acid responds to all the tests, and what *was* colloidal sulphur to none of them.

The solution containing pentathionic acid used in the above experiments was obtained by adding 10 c.c. of 2*N*-hydrochloric acid to 10 c.c. of *N*-cupric chloride, followed by 20 c.c. of 2*N*-sodium thiosulphate, concentrating to half the volume, and filtering from cuprous sulphide, the last two operations being repeated after the addition of another 10 c.c. of 2*N*-hydrochloric acid: a clear, colourless, acid solution remained. Valeten's statement may be modified by saying that pentathionic acid, when rendered alkaline, liberates colloidal sulphur.

Relative Stability of Pentathionic Acid and its Salts.—Watson Smith (T., 1883, 43, 355) maintained that pentathionic acid is stable, but that its salts are not, since they readily decompose, yielding sulphur and tetrathionates. This difference between the acid and its salts was recognised by Debus (*loc. cit.*) and by other workers, including Riesenfeld and Fell (*loc. cit.*), who attempt to account for it on their theory, which involves "the hydrate of SO_2 ." This is stable in acid solution and polymerises to produce pentathionic acid. The theory appears to be a variant of Debus's hypothetical S_2O_2 , which polymerises and then combines with water: $5\text{S}_2\text{O}_2 = 2\text{S}_5\text{O}_5$ and $\text{H}_2\text{O} \div \text{S}_5\text{O}_5 = \text{H}_2\text{S}_5\text{O}_6$. Our interpretation of the matter is simply that the molecule of pentathionic acid is fairly stable, whilst its possible anions are very unstable. The following observations bear out this view:

i. On several occasions it was noticed that perfectly clear filtrates in Wackenroder preparations were rendered turbid by addition of pure water (dilution favouring ionisation).

ii. We find that any reagent that develops alkalinity immediately precipitates sulphur from pentathionic acid (salt formation).

iii. Solutions containing pentathionic acid in a slight excess of mineral acid slowly decompose in the cold with formation of sulphuric acid, deposition of sulphur, and evolution of sulphur dioxide, but in fairly concentrated mineral acid the solution may be boiled for several hours without separation of sulphur.

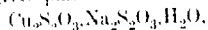
The potassium and barium salts were prepared by Lewis (T., 1881, 39, 68), who found that the pure salts could be obtained from highly concentrated solution only, and Shaw (T., 1883, 43, 351) obtained potassium pentathionate, apparently pure, only from his sixth and last crop of crystals. It seems to be a matter of great difficulty to obtain these simple pentathionates in the pure state.

These results are all in keeping with the theory of ionic dissociation coupled with the assumption that HS_5O_6^- or $\text{S}_5\text{O}_6^{2-}$ (or both ions) is very unstable.

Summary.

1. Cupric salts are reduced at once to the cuprous state on adding excess of sodium thiosulphate. From normal or more concentrated solution, the yellow salt, $3\text{Cu}_2\text{S}_2\text{O}_3 \cdot 2\text{Na}_2\text{S}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$, crystallises out rapidly. Sodium tetrathionate is simultaneously produced.

2. When copper nitrate is used, pure specimens of the yellow salt are obtained. With copper sulphate, the yellow salt contains $3\text{Cu}_2\text{SO}_4 \cdot 2\text{Na}_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ in solid solution. With copper chloride, the yellow salt soon gives place to the white salt,



which invariably contains $\text{Cu}_2\text{Cl}_2 \cdot 2\text{NaCl} \cdot \text{H}_2\text{O}$ in solid solution. The yellow salt in this case was found to be a mixture containing some of the white salt.

3. The pure yellow salt is quite stable if kept dry and prepared perfectly free from adhering tetrathionate. When strongly heated, it yields cuprous sulphide and sodium sulphate, whilst sulphur, sulphur dioxide, and water are expelled.

4. A white salt, $2\text{Cu}_2\text{S}_2\text{O}_3 \cdot 3(\text{NH}_4)_2\text{S}_2\text{O}_3 \cdot \text{H}_2\text{O}$, has been obtained from concentrated solutions containing copper nitrate and ammonium thiosulphate.

5. When copper salts in presence of excess of thiosulphates are heated with mineral acids, cuprous sulphide is precipitated, but this precipitation is not complete even after prolonged boiling if hydro-

chloric acid is employed. The reason for this appears to depend on the formation of the double chloride mentioned above, which cannot decompose into cuprous sulphide. The precipitation is complete if nitric acid is used, provided the acid concentration is less than $N/2$, and is complete with sulphuric acid, which should be fairly concentrated if any copper chloride is present.

6. In the above circumstances, pentathionic acid is produced through the interaction of thiosulphate, tetrathionate, and mineral acid.

7. We have examined previous work on pentathionic acid and its salts and have indicated some methods of differentiating pentathionic acid from colloidal sulphur. We conclude that the molecule $H_2S_5O_6$ is stable, especially in presence of high concentration of hydrogen-ions, but that its salts are very unstable, because they tend to ionise, and we believe the anions HS_5O_6' and S_5O_6'' to be very unstable.

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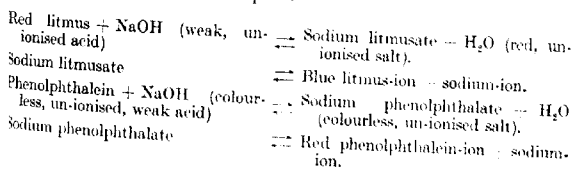
[Received, March 24th, 1923.]

(C.L.—*The Sodium Salts of Phenolphthalein.*

By HENRY BASSETT and PHILIP HALTON.

THE cause of the colour changes observed with indicators on addition of acid or alkali is of great theoretical interest and practical importance, but it is still shrouded in obscurity.

The first attempted explanation was due to Ostwald ("Wissenschaftlichen Grundlagen der Analyt. Chemie," 1894, 1st ed.), who suggested that the free indicator, a very weak acid, was practically un-ionised, and had one colour, whilst the ions obtained from the alkali salt had another colour. The un-ionised alkali salt would have the same colour as the free indicator but, as it is nearly completely ionised in dilute solutions, a sharp colour change is obtained on addition of a small amount of alkali to a neutral solution of the indicator. Thus, to take the case of litmus and phenolphthalein as examples:



On addition of acid the colour changes are reversed, owing to

combination of the coloured ions with hydrogen-ion derived from the added acid and formation of the un-ionised indicator acid.

The work of Hantzsch and other investigators has, however, shown that ionisation *per se* probably never gives rise to colour changes, and that when colour changes do occur in salt formation they are associated with some structural change in the molecules concerned.

The free indicator has one structure and is either non-acid or only very feebly so, whilst the alkali salt is derived from an isomeric form of the indicator which is more strongly acid, but in the free condition is metastable. This acidic form of the indicator, its alkali salts, and its anion all have the colour shown by the alkaline solutions. In solution these possible forms are in equilibrium thus:

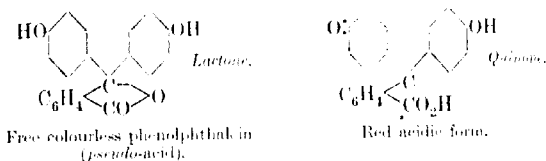
Red neutral form of litmus \rightleftharpoons Blue litmus acid \rightleftharpoons Blue litmus anion + H-ion.

Colourless neutral form of phenolphthalein \rightleftharpoons Red phenolphthalein acid \rightleftharpoons Red phenolphthalein ion + H-ion.

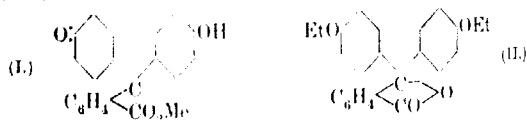
Alkali shifts these equilibria from left to right, whilst acid shifts them in the opposite direction.

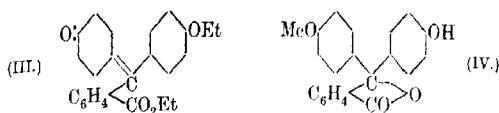
In the case of indicators which are of a basic instead of acidic character precisely similar arguments to the above apply.

In the case of phenolphthalein, the isomerism is between a benzenoid and a quinonoid form, the latter being red (Stieglitz, *J. Amer. Chem. Soc.*, 1903, **25**, 1112; see also Friedländer, *Ber.*, 1893, **26**, 172; H. E. Armstrong, *P.*, 1893, **9**, 52).



The experimental evidence so far as it goes supports these views. Several methyl derivatives have been obtained. Thus Green and King (*Ber.*, 1907, **40**, 3724; *P.*, 1907, **23**, 228) obtained a mono-methyl ester crystallising in orange needles. It forms a violet-red solution in alkali hydroxides from which the unchanged methyl ester is obtained by immediate acidification, and phenolphthalein by postponed acidification. Formula I is attributed to this ester.

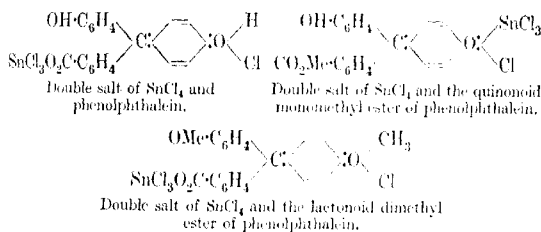




Haller and Guyot (*Compt. rend.*, 1895, **120**, 296) have prepared the colourless diethyl ester (II). The corresponding dimethyl ester was originally prepared by Beyer (*Annalen*, 1880, **202**, 36) and more fully investigated by Grande (*Gazzetta*, 1896, **26**, i, 222; see also Herzig and Meyer, *Ber.*, 1895, **28**, 3258).

Meyer and Marx (*Ber.*, 1907, **40**, 3603) obtained the isomeric diethyl ester (III) as intensely yellow crystals. The colourless monomethyl ester (IV), isomeric with the quinonoid ester (I), has been prepared by Meyer and Spengler (*Ber.*, 1905, **38**, 1318). In alkalis, it yields a faintly red solution, the colour of which is weaker the purer the ester (Green and King, *loc. cit.*). The corresponding monomethyl ester was prepared by Grande (*Ann. Chim. Farm.*, 1892, **14**, 331). The orange dimethyl ester corresponding to the yellow diethyl ester (III) was obtained by Green and King (*loc. cit.*), who found that it was insoluble in alkali.

Phenolphthalein itself, its quinonoid monomethyl ester (I), and its lactonoid dimethyl ester (II) all form cinnabar-red additive compounds with hydrogen chloride, stannic chloride, and aluminium chloride, which are formulated as quinonoid oxonium salts by Meyer and Hantzsch (*Ber.*, 1907, **40**, 3479), thus:



Very similar compounds have been prepared from tetrabromophenolphthalein and from quinolphthalein (see, for instance, Meyer and Spengler, *loc. cit.*; Green and King, *loc. cit.*; Meyer and Marx, *Ber.*, 1907, **40**, 1437).

It will be seen from the above *résumé* that the position with regard to the esters of phenolphthalein is fairly satisfactory, and explicable in terms of the usually accepted benzenoid-quinonoid isomerism of phenolphthalein. The position with regard to the alkali salts is very different, however. In the literature on the

subject one comes across references to the solid red salts of phenolphthalein, but on examination of the original papers no case of the isolation of a red salt could be found. Meyer and Marx (*Ber.*, 1908, **41**, 244) evaporated solutions of phenolphthalein in sodium and potassium hydroxides, obtaining deep red, sticky masses, but were unable to obtain any salt in a crystalline state. Meyer and Spengler (*Ber.*, 1908, **38**, 1318) considered that they had proved that the red salt of phenolphthalein was the disodium salt by digesting 20 c.c. of *N*-caustic soda solution with excess of phenolphthalein, removing the excess by filtration, and determining the ratio of sodium to phenolphthalein in the solution. This ratio they found to be that of two atoms of sodium to one molecule of phenolphthalein, and, overlooking the fact that since the latter behaves as a very weak acid there would be a large amount of hydrolysis in solution, they claimed to have proved that the red salt was the disodium salt. This so-called proof has been accepted by some investigators (for example, Acree and Slagle, *Amer. Chem. J.*, 1909, **42**, 115; Kober and Marshall, *J. Amer. Chem. Soc.*, 1911, **33**, 59), but it is clearly not valid.

Oddo and Vassallo (*Gazzetta*, 1912, **42**, ii, 204) claim to have obtained a red monopotassium salt of phenolphthalein by adding a hot saturated alcoholic solution of potassium hydroxide to a hot saturated alcoholic solution of phenolphthalein and leaving to stand for twenty-four hours in a vacuum. On repeating this experiment, using the quantities of materials stated in the paper, an abundant yield of small crystals was obtained. After separation from the red mother-liquor and washing with alcohol (as stated in the paper), the crystals were found to be white and not reddish-violet, as stated by Oddo and Vassallo. The crystals very rapidly absorbed moisture from the air, turning a pale pink. Under the microscope, they were seen to be colourless rhombs. On analysis, they were found to contain 1 atom of potassium to 1.007 molecules of phenolphthalein.

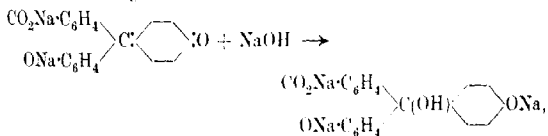
Haller and Guyot (*loc. cit.*), by heating the colourless, lactonoid diethyl ester of phenolphthalein with alcoholic potash, obtained white needles of the salt $\text{CO}_2\text{K}\cdot\text{C}_6\text{H}_4\cdot\text{C}(\text{C}_6\text{H}_4\cdot\text{OEt})_2\cdot\text{OH}$. No analytical figures were given by them. Kober and Marshall (*J. Amer. Chem. Soc.*, 1911, **33**, 59, 1779) isolated colourless trisodium and tripotassium salts by concentrating saturated solutions of phenolphthalein in strong aqueous caustic soda and caustic potash. The formulæ $\text{CO}_2\text{K}\cdot\text{C}_6\text{H}_4\cdot\text{C}(\text{C}_6\text{H}_4\cdot\text{OK})_2\cdot\text{OH}\cdot 5\text{H}_2\text{O}$ and $\text{CO}_2\text{Na}\cdot\text{C}_6\text{H}_4\cdot\text{C}(\text{C}_6\text{H}_4\cdot\text{ONa})_2\cdot\text{OH}\cdot 6\text{H}_2\text{O}$ are ascribed to these salts, but the method of isolation makes one feel some doubt about their actual composition, especially in respect to the amount of water of

crystallisation. The sodium salt is described as crystallising in rhombohedra. Kober, Marshall, and Rosenfeld (*J. Amer. Chem. Soc.*, 1912, **34**, 1424) obtained the colourless monopotassium salt containing one molecule of water and one molecule of alcohol of crystallisation, $\text{CO}_2\text{K}\cdot\text{C}_6\text{H}_4\cdot\text{C}(\text{C}_6\text{H}_4\cdot\text{OH})_2\cdot\text{OH}\cdot\text{H}_2\text{O}\cdot\text{C}_2\text{H}_5\text{O}$, as also the corresponding sodium salt. This was done by passing carbon dioxide into a solution of the tripotassium or trisodium salt in absolute alcohol, filtering the product, and precipitating with dry ether. They are described as forming colourless, hexagonal prisms with truncated ends.

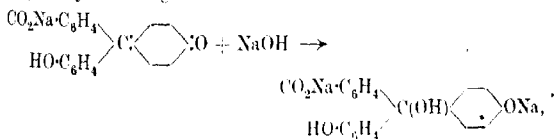
That excess of alkali decolorises red phenolphthalein solution is well known (Bayer, *Annalen*, 1880, **202**, 36). It seemed to support Ostwald's view of the colour changes. The excess of sodium-ion, by throwing back the ionisation of the sodium salt of phenolphthalein, removed the red ions to which the colour was due. Green and Perkin (*L.*, 1904, **85**, 398) showed, however, that this explanation of the bleaching effect of excess alkali could not be correct, and for two reasons. In the first place, the bleaching is a time phenomenon, and in the second place the decolorised solutions can be rendered neutral to litmus by careful addition of acetic acid in the cold without the colour returning. When this point is reached, it is found that alkali and phenolphthalein are present in solution in the proportions required for the monosodium or monopotassium salt.

After standing for some time or more quickly by boiling, these so neutralised solutions again become coloured, and the remaining alkali can be titrated in the usual way. It is worthy of note that a precisely similar behaviour is shown by many other triphenylmethane dyes.

Although these facts do not fit in with Ostwald's theory, they are in no way opposed to the theory which ascribes the colour changes to tautomerism between a colourless, lactonoid form and a red, quinonoid form. The bleaching effect of excess of alkali would be due to the change



or possibly the change

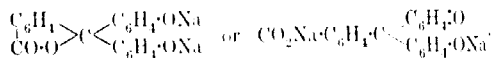


and it is quite likely that such an addition would be comparatively slow. On neutralisation with acetic acid in the cold, the phenolic sodium atoms would be displaced, leaving the colourless carboxylic salt. The latter then slowly loses water and yields the quinonoid salt.

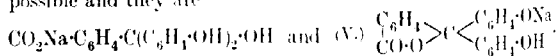
The present investigation was undertaken in the hope that a phase-rule study of the system phenolphthalein-caustic soda-water might throw considerable light on the whole question. In any case, it seemed the only way in which definite information could be obtained as to the sodium salts of phenolphthalein which actually exist. It is rather remarkable, in fact, that no such examination of an indicator-alkali-water system (or, more generally, of a dye-alkali-water system) has so far been made.

The system is a three-component one, and has been studied at a temperature of 25°. The most striking result of the investigation is that a red sodium salt is apparently incapable of existing as a solid phase in contact with solution at this temperature. All the salts obtained are colourless. They are respectively (a) two monosodium salts with four and eight molecules of water of crystallisation; (b) three disodium salts, of which one is anhydrous and the other two contain 4 and 8 molecules of water, respectively; (c) four trisodium salts with 6, 12, 13, and 14 molecules of water of crystallisation.

All the trisodium salt hydrates are stable over definite ranges of concentration at 25°, but of the disodium compounds only the octahydrate is stable, the other two being metastable. Of the two monosodium salts, only the tetrahydrate is stable. The results are perfectly sharp and definite, as can be seen from the annexed triangular and rectangular diagrams. The existence of a crystalline, anhydrous disodium salt is of considerable importance. Such a salt could only be either



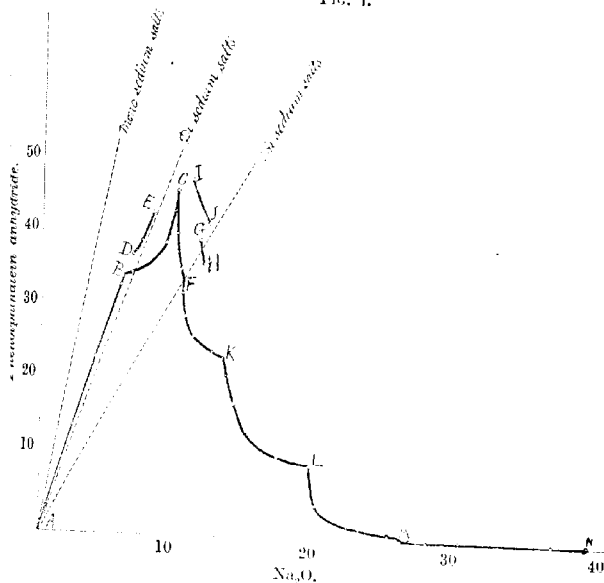
and as it is colourless it must be regarded as the diphenolic salt. This makes it highly probable that the two hydrated forms of the disodium salt also have the phenolic structure. For the trisodium salt, there is only one possible structure, namely, $\text{CO}_2\text{Na} \cdot \text{C}_6\text{H}_4 \cdot \text{C}(\text{C}_6\text{H}_4\text{ONa})_2 \cdot \text{OH}$, but two monosodium salts are possible and they are



There can be little question that the colourless monosodium salt obtained in solution by neutralisation of the colourless solutions of

the trisodium salt with acetic acid is the carboxylic salt and it follows from this that the acid $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{C}(\text{C}_6\text{H}_4\cdot\text{OH})_2\cdot\text{OH}$ is, as regards the carboxylic hydrogen, probably a stronger acid than acetic acid. In all probability, however, the solid hydrated monosodium salts which have been obtained in the present investigation have the phenolic structure (V).

Fig. 1.

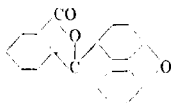
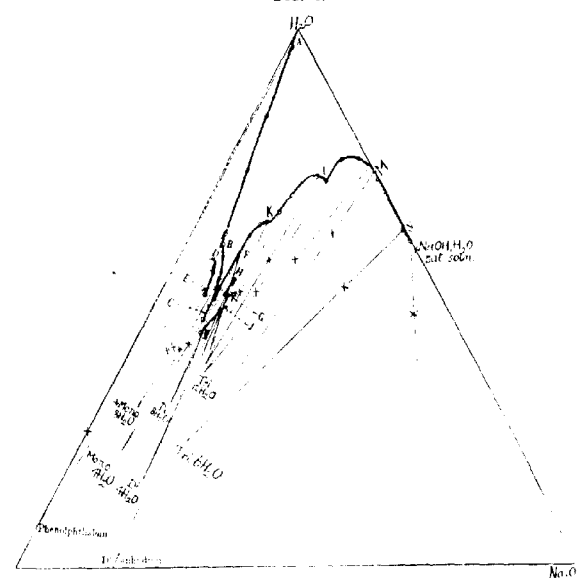


CURVE AND SOLID PHASE.—AB, Phenolphthalein; BC, Mono-sodium salt + $4\text{H}_2\text{O}$; DE, Mono-sodium salt + $8\text{H}_2\text{O}$; CF, Di-sodium salt + $8\text{H}_2\text{O}$; GH, Di-sodium salt + $4\text{H}_2\text{O}$; IJ, Di-sodium salt (anhydrous); FK, Tri-sodium salt + $14\text{H}_2\text{O}$; KL, Tri-sodium salt + $13\text{H}_2\text{O}$; LM, Tri-sodium salt + $12\text{H}_2\text{O}$; MN, Tri-sodium salt + $6\text{H}_2\text{O}$.

It might at first be thought that this follows from the enormous extent to which they are apparently hydrolysed in aqueous solution. A glance at the rectangular diagram will show how great this is. The three dotted lines on that diagram are drawn through points corresponding to solutions containing Na_2O and phenolphthalein in proportions corresponding respectively to pure mono-, di-, and tri-sodium salts. It will be seen that before the monosodium salt can be separated as a solid phase the solution must contain nearly twice the proportion of alkali needed to form the monosodium salt.

Only in the case of the trisodium salt can a saturated solution be obtained which contains comparatively little more alkali than is stoichiometrically required. This point, *F*, on the diagram corresponds to the presence of 3.2 molecules of sodium hydroxide to 1 molecule of phenolphthalein. It is worth noting, however,

FIG. 2.



CURVE AND SOLID PHASE.—AB, *Phenolphthalein*; BC, *Mono-sodium salt* + 4H₂O; DE, *Mono-sodium salt* + 8H₂O; CF, *Di-sodium salt* + 8H₂O; GH, *Di-sodium salt* + 4H₂O; IJ, *Di-sodium salt* (anhydrous); FK, *Tri-sodium salt* + 14H₂O; KL, *Tri-sodium salt* + 13H₂O; LM, *Tri-sodium salt* + 12H₂O; MN, *Tri-sodium salt* + 6H₂O.

that in all cases the actual apparent hydrolysis is probably greater than appears from the diagrams, for in such concentrated solutions a great deal of the water may not be present as "free" water.

Now it has been shown by Shields (*Phil. Mag.*, 1893, [v], 35, 365) that even in decinormal solution sodium acetate is only hydrolysed to the extent of 0.008 per cent. at 25°, and, as is well known, there

is no difficulty in obtaining solutions of sodium acetate saturated with respect to the solid salt. Such solutions are faintly alkaline to litmus. Were the monosodium salts which separate from the alkaline phenolphthalein solutions actually carboxylic salts, such extensive hydrolysis as that apparently found would not be expected in view of the fact that the carboxylic acid is probably stronger than acetic acid for the reason given above. From the behaviour of strongly alkaline phenolphthalein solutions on titration with hydrochloric acid (see experimental part) it is highly probable that the carboxylic acid is much stronger than acetic acid.

As pointed out at the end of the theoretical section of this paper, however, great caution is required in drawing any conclusions from the apparent extensive hydrolysis of the sodium salts. The chief reason for concluding that the solid colourless monosodium salt obtained really has the lactone phenolic structure is that it separates from solutions intermediate between those from which phenolphthalein itself separates and those from which the disodium salts separate: the former must be saturated with respect to the lactone phenolphthalein itself, and the latter with respect to its disodium salt. It almost follows from this that the intermediate solutions will be saturated with respect to the lactone phenolic monosalt. Although no red salt has been obtained in a solid state, it clearly exists in solution, and almost certainly has the tautomeric quinonoid structure. One must suppose that in the alkaline solutions there is an equilibrium between the coloured quinonoid salts, the colourless carboxylic salts, the colourless lactonoid salts, and free phenolphthalein both as lactone and as the red and the colourless carboxylic acid. Each of these will, in addition, be in equilibrium with its ions. Some or all of the compounds in this list will be present in any given solution in proportions depending on the concentration and temperature.

The compounds thus concerned may be summarised as follows:

- A. $\begin{array}{c} \text{C}_6\text{H}_4 \\ \text{CO}\cdot\text{O} \end{array} > \text{C}(\text{C}_6\text{H}_4\cdot\text{OH})_2$ and $\begin{array}{l} \text{one mono-salt} \\ \text{one di-salt} \end{array}$
All colourless.
- B. $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{C}(\text{C}_6\text{H}_4\cdot\text{OH})_2\cdot\text{OH}$ and $\begin{array}{l} \text{one mono-salt}^* \\ \text{one di-salt}^* \\ \text{one tri-salt} \end{array}$
All colourless.
- C. $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{C} \begin{array}{c} \text{C}_6\text{H}_4\cdot\text{OH} \\ \text{C}_6\text{H}_4\cdot\text{O} \end{array}$ and $\begin{array}{l} \text{one mono-salt}^* \\ \text{one di-salt} \end{array}$
All coloured.

* If all the acidic hydrogen atoms are not replaced by sodium, it is practically certain that the carboxylic hydrogen will be one that is replaced. If this is not granted, then an additional salt becomes possible in the cases marked (*).

It will be seen that the conditions holding in alkaline phenolphthalein solutions are very complex, especially in the region where the mono- or di-salts can separate as solid phases. It is not possible to say what proportions of the various compounds mentioned above are present in such solutions, but judging by the very deep red colour of the solutions in the mono-di-region they contain a large proportion of the quinonoid forms. The question has to be considered why such red salts do not separate in the solid form. What compound can separate from such a solution will depend on the magnitude of its solubility product and on the concentration in which it is present, both in ionised and un-ionised form in the solution. It must be assumed that the concentration of the quinonoid form is not sufficient for separation of the solid red salt from solution to be possible. Owing, moreover, to the complicated state of affairs in the alkaline solutions, care is necessary in drawing conclusions from the solubility curves as to the degree of hydrolysis of individual salts. The curves do show that the apparent hydrolysis is very great, but this apparent hydrolysis is a summation effect of several hydrolytic decompositions and other equilibria (such as between lactone and carboxylic or quinonoid forms). The use of phenolphthalein as an indicator depends on this apparent large hydrolysis, which corresponds to apparent extreme weakness of the indicator acid. Most of the individuals concerned in the phenolphthalein equilibria may, however, be relatively strongly acidic. The chief function of the large excess of sodium hydroxide needed for a solution to be in contact with any particular sodium salt may be not so much to repress hydrolysis as to supply a sufficient concentration of sodium-ions for the solubility product of the particular salt to be reached.

EXPERIMENTAL.

Mixtures of phenolphthalein with solutions of caustic soda of varying strengths were made up so that in each case a liquid and a solid phase were obtained. Freshly boiled, distilled water was used in all cases. The weak solutions of caustic soda were made by Cornog's method (*J. Amer. Chem. Soc.*, 1921, **43**, 2573). A known volume of water was placed in a glass bottle, covered with a layer of ether about 2 cm. deep, and a known weight of sodium dropped in piece by piece. After solution of the sodium, the major part of the ether was removed with a pipette, and the last traces were driven off by heating on a water-bath. The necessary amount of phenolphthalein was then added and the tightly fitting stopper placed in position and fastened down with string and wax.

The stronger solutions of caustic soda were made by placing a known weight of sodium in a platinum crucible, which was supported

on a triangle in a desiccator containing water. On exhausting the desiccator with a water-pump, the sodium gradually dissolved. Any further water required to make up the solution of the required strength was then added. The solution together with the necessary amount of phenolphthalein was placed in a cerasin wax bottle, the lid of which was then sealed on. Great accuracy had to be used in making up the contents of the bottles when it was desired to obtain points in any special region of the system. The bottles were rotated in a thermostat, kept at 25°, in such a way that the contents were well shaken.

After being in the thermostat for not less than three days, which time was found sufficient for the attainment of equilibrium between solid and solution, the bottles were opened and the solid and liquid separated and analysed.

In most cases, the liquid was filtered off, but in the case where the anhydrous disodium salt was obtained as solid phase the liquid was too viscous for this, but as the solid was deposited in spherulitic growths on the sides of the containing vessel, the liquid was separated by decantation. The filtration was carried out in a simple apparatus below the surface of the water in the thermostat in order to prevent cooling. With some of the more viscous solutions many hours were needed to obtain sufficient liquid for analysis, so that such a precaution was absolutely essential. A so-called "oil bottle" which has a cup-like expansion above the neck was fitted with a two-holed rubber bung. Through one hole passed a glass tube for use in exhausting the bottle. Through the other passed the stem of a wide glass tube filtering funnel, which was fitted with a perforated porcelain disk and a dry asbestos filtering pad. Mercury was placed in the cup of the bottle so as to make a water-tight seal, and the apparatus held immersed in the thermostat by a clamp on the upper part of the filtering tube. Some of the mixture to be filtered was rapidly transferred to the filter tube, which was then tightly corked to exclude carbon dioxide, and gentle suction was applied by means of the water-pump. The clear filtrate was caught in a weighed test-tube placed in the oil bottle, whilst the moist solid was removed from the filter tube by means of a long spatula and transferred to a weighing bottle. The analyses were carried out as follows. Weighed amounts of solution or moist solid were placed in beakers together with water and heated to boiling, standard hydrochloric acid being added until the colour was discharged. The amount of acid used gave the percentage of soda. The phenolphthalein, which separated out in a crystalline state, was collected on a Gooch crucible, well washed, and dried in a steam-oven to constant weight. In some cases, the precipitated phenolphthalein

was slightly discoloured owing to the presence of traces of (apparently) oxidation products. It was found that the titration with acid could not be satisfactorily performed in the cold. In that case, the colour disappeared but was restored on standing or heating. By adding more acid, the colour was again discharged, and on repeating the process at intervals the same end-point was eventually reached as by the hot titration method. The behaviour was analogous to that observed by Green and Perkin with acetic acid (*loc. cit.*) and is due to the formation of the colourless monosodium carboxylic salt. It indicates what a comparatively strong acid the carboxylic acid must be.

The moist solids were always examined under the microscope. In most cases, it was easy to see that the solid was colourless. In others, where the solution was very deeply coloured and very viscous, it was more difficult. Even in such cases, however, isolated crystals in air bubbles or round the edges of the slide were seen to be definitely colourless. No coloured salt was obtained.

The monosodium salt with $4\text{H}_2\text{O}$ was seen to be in the form of short, rhombic prisms, whilst the octahydrate formed long, rhombic prisms. The anhydrous disodium salt was obtained in colourless, spherulitic growths on the sides of the glass bottle. The tetrahydrated disodium salt and the trisodium salts with 14, 13, and 12 molecules of water of crystallisation occurred as stumpy, rhombic prisms, whilst the disodium salt with $8\text{H}_2\text{O}$, and the hexahydrated trisodium salt occurred in long, needle-shaped crystals. In all cases, the crystals were very small.

The compositions of the solids and equilibrium solutions analysed are given in the table and are expressed in terms of H_2O , Na_2O , and $\text{C}_{30}\text{H}_{12}\text{O}_3$ (the anhydride of phenolphthalein), the water of course being obtained by difference.

The percentage compositions of the equilibrium solutions and of the corresponding moist solids have been plotted in triangular co-ordinates, and the formulae of the corresponding dry solids are obtained at once from the diagram by Schreinemaker's well-known method. This is the only sure way of determining the nature of the solids in a dry state in most cases. The compositions of the solutions have also been plotted in rectangular co-ordinates, as the diagram so obtained is in some ways easier to follow. It will be seen from the diagrams that the solubility of phenolphthalein increases rapidly with increasing concentration of sodium hydroxide. So also do the colour and the viscosity of the solutions. Solutions in equilibria with solid phenolphthalein contain slightly less than 2 molecules of caustic soda per molecule of dissolved phenolphthalein. At a concentration of 33.2 per cent. of phenolphthalein anhydride

TABLE.

Composition of phases in the system phenolphthalein-sodium hydroxide-water at 25°.

Liquid phase.			Moist solid phase.		
Na ₂ O. Per cent.	Phenol- phthalein anhydride. Per cent.	H ₂ O. Per cent.	Na ₂ O. Per cent.	Phenol- phthalein anhydride. Per cent.	H ₂ O. Per cent.
Solid phase : Phenolphthalein (curve <i>AB</i> on diagrams).					
0.58	2.90	96.58	0.30	79.56	20.15
2.71	13.74	83.54	1.15	84.67	14.18
4.25	22.43	73.31	1.61	68.90	29.49
6.11	31.96	61.91	2.45	69.28	28.26
Solid phase : Monosodium salt + 8H ₂ O (curve <i>DE</i> on diagrams).					
6.65	30.06	56.99	6.97	55.08	37.95
7.48	37.73	54.79	6.77	58.21	35.02
8.32	41.16	50.52	7.41	53.55	39.04
Solid phase : Monosodium salt + 4H ₂ O (curve <i>BC</i> on diagrams).					
6.78	33.34	59.88	6.33	47.74	45.93
9.31	37.36	53.33	8.58	52.16	39.26
9.88	41.45	48.67	9.30	49.77	40.93
10.06	44.06	45.88	9.56	49.63	40.81
Solid phase : Disodium salt, anhydrous (curve <i>IJ</i>).					
11.00	45.55	43.45	11.17	46.77	42.06
12.31	40.16	47.53	12.56	43.42	44.02
Solid phase : Disodium salt + 4H ₂ O (curve <i>GH</i>).					
11.67	37.79	50.54	12.51	45.19	42.30
11.98	34.68	53.34	12.46	43.69	43.85
Solid phase : Disodium salt + 8H ₂ O (curve <i>CF</i>).					
9.97	38.42	51.61	10.93	42.45	46.62
10.17	33.72	56.11	11.17	47.42	41.41
Solid phase : Trisodium salt + 14H ₂ O (curve <i>FK</i>).					
10.24	31.00	58.76	13.25	41.16	45.59
10.37	27.89	61.76	12.38	38.87	48.73
11.34	25.03	63.62	12.97	38.68	48.35
12.69	23.28	64.03	13.20	32.63	54.17
Solid phase : Trisodium salt + 13H ₂ O (curve <i>KL</i>).					
13.73	20.51	65.76	14.23	40.59	45.18
14.29	16.91	68.80	14.46	46.01	39.53
17.48	10.35	72.97	16.13	28.56	55.31
Solid phase : Trisodium salt + 12H ₂ O (curve <i>LM</i>).					
19.8	9.12	71.08	16.65	35.67	47.68
20.32	4.28	75.39	17.49	31.69	50.79
23.46	1.37	75.17	18.66	29.39	51.95
25.42	0.86	73.72	20.33	25.40	54.27
Solid phase : Trisodium salt + 6H ₂ O (curve <i>MX</i>).					
27.01	0.11	72.88	25.04	13.16	61.80
28.03	0.0	71.97	26.37	10.89	62.74
30.74	0.0	69.26	28.32	11.48	60.20
37.44	0.23	62.56	31.47	17.93	50.60
* 39.88	0.0	60.12	46.97	6.37	46.66

* Solid phase—mixture of trisodium salt hexahydrate and NaOH.H₂O.

and 6.3 per cent. of Na_2O the solubility curve of phenolphthalein cuts the curve of the monosodium tetrahydrate, which is the stable solid phase until a concentration of 44.06 per cent. of phenolphthalein anhydride and 10.06 per cent. of Na_2O is reached, when the disodium salt with eight molecules of water of crystallisation begins to separate. From this point, the solutions become weaker and weaker with respect to phenolphthalein as the content of alkali increases, whilst the colour gradually gets weaker. At 32.1 per cent. of phenolphthalein anhydride and 10.5 per cent. of Na_2O the trisodium salt with 14 molecules of water becomes the stable solid phase. At successively greater Na_2O -concentrations, the 13-, 12-, and 6-hydrates of the trisodium salt become the stable phases until, at 39.88 per cent. of Na_2O , the solution, which contains the merest trace of phenolphthalein, is saturated with respect to a mixture of the hexahydrated trisodium salt and the monohydrate of sodium hydroxide, $\text{NaOH}\cdot\text{H}_2\text{O}$. The saturated solution of $\text{NaOH}\cdot\text{H}_2\text{O}$ in pure water at 25° contains 41.2 per cent. of Na_2O (Pickering, *T.* 1893, **63**, 890). As will be seen from the diagrams, the monosodium salt with $8\text{H}_2\text{O}$ and the anhydrous disodium salt, as well as its tetrahydrate, are metastable phases.

Summary.

A phase-rule study of the system phenolphthalein-caustic soda-water has been made at 25° .

A number of crystalline sodium salts have been obtained, all of which are colourless. These are, two hydrated forms of a monosodium salt, a disodium salt in the anhydrous form and as two different hydrates, and four different hydrates of the trisodium salt.

The nature of the solid salts and of the solutions is discussed. None of the facts observed is opposed to the theory of benzenoid-quinonoid tautomerism of phenolphthalein derivatives.

UNIVERSITY COLLEGE, READING.

[Received, March 24th, 1923.]

CLI.—*The so-called Pre-pressure Interval in Gaseous Explosions.*

By JOHN DAVID MORGAN.

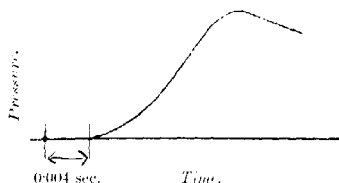
WHEN an explosive gaseous mixture, contained in a closed vessel, is ignited by an electric spark, and records are made of the passage of the spark and of the rise of explosion pressure, it is found that the commencement of rise of pressure occurs, not simultaneously

with the passage of the igniting spark, but later, the two events being separated by a relatively large interval of time. This fact is well known (Bairstow and Alexander, *Proc. Roy. Soc.*, 1905, [A], 76, 340; Wheeler, T., 1918, 113, 840; Morgan, *Engineering*, 1919, 535; David, *Engineering*, 1922, 791; Woodbury, Lewis, and Canby, *J. Soc. Automotive Engineers, U.S.A.*, 1921, 8, No. 3; Payman, "Fuel in Science and Practice," March, 1922), and the interval is usually referred to as the no-pressure or pre-pressure interval. A typical pressure-time diagram is shown in Fig. 1.

That the flame originates with the passage of the spark has been definitely established (Morgan, *loc. cit.*) and it has been shown by Wheeler (*loc. cit.*) and, by Woodbury, Lewis, and Canby (*loc. cit.*) that before any indication of pressure occurs the flame has advanced through a considerable volume of the gas.

It has been suggested that the so-called pre-pressure interval is an apparent effect due to insufficient sensitiveness of the pressure

FIG. 1.



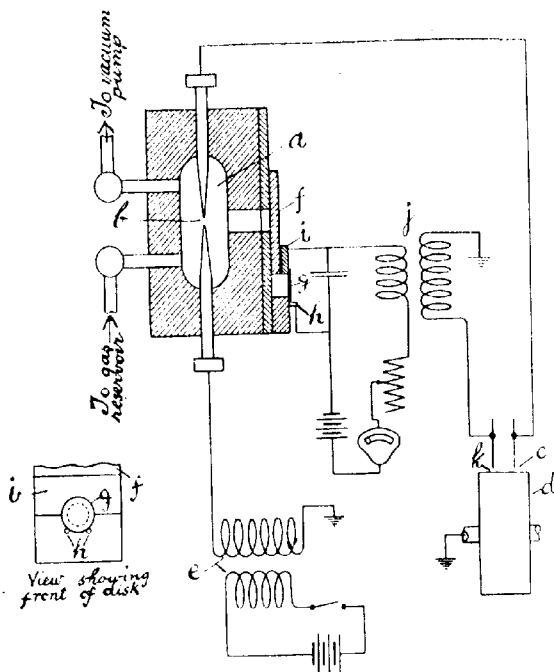
indicator, and some evidence has been adduced to show that the interval can be attributed at least in part to the indicator (Morgan, *loc. cit.*). Arguing from established facts relating to the inflammation of gaseous mixtures in a closed vessel, Payman concludes that the term "pre-pressure" interval is a misnomer, "since during a considerable proportion of this period the pressure is actually increasing" (Payman, *op. cit.*).

The question as to whether or not the pre-pressure interval is a real effect associated with the explosion is of some importance. For example, in assigning an algebraic expression to the rising part of the pressure curve it is necessary to know whether the origin should be taken at the instant of passage of the spark or at the apparent commencement of pressure on the diagram.

A recent re-examination of the question leads to the conclusion that the pre-pressure interval, as ordinarily observed, is due mainly to the indicator. That some interval must occur between the passage of the spark and the first indication of pressure is evident, as the rate of travel of a pressure pulse is finite. This interval is, however, much smaller than the one under consideration.

The means employed in the investigation are shown in Fig. 2. An explosion chamber, *a*, is fitted with an igniting spark gap, *b*, in series with a small gap, *c*, formed between a needle point and a smoked paper strip on an earthed metal drum, *d*. The spark at *b* is produced by a small induction coil, *e*, when the primary circuit of that coil is opened, and simultaneously a spark occurs at *c*,

FIG. 2.



making a small mark on the smoked strip. A hole in one side of the explosion chamber communicates with a contact breaker carried on a slide, *f*. This contact breaker consists of a small and very light silver disk, *g* ($\frac{3}{8}$ inch in diameter), supported on a pair of contact pegs, *h*, and arranged to lean against the outer face of an insulated contact piece *i*. The parts *h* and *i* are connected to the primary of another induction coil, *j*, the secondary of which is connected to a second spark gap, *k*, at the drum. A

condenser is arranged across the contacts *h*, *i* to suppress sparking at the disk, and a variable resistance and an ammeter are provided in a primary circuit, so that, if necessary, the current prior to each experiment can be adjusted to a predetermined amount.

After the slide has been moved downwards to cover the hole in the explosion chamber the latter is exhausted, and a charge of previously prepared gas mixture is admitted. The slide is then returned until the contact breaker disk is opposite the hole, and the gas is ignited by a spark at *b*. A record of this spark is made by the simultaneous spark at *c*. As soon as the pressure pulse due to the development of flame reaches the contact breaker disk, it blows the disk away, and by interrupting the primary current in the coil, *j*, causes a recording spark to occur at the second gap, *k*. Thus two records are obtained, one corresponding to the passage of the igniting spark and the other to the attainment of sufficient explosion pressure to displace the contact breaker disk.

The device is extremely sensitive, and it was found that the pressure pulse due solely to the passage of the igniting spark was sufficient to operate the disk. Consequently the explosion chamber had to be inclined sufficiently to allow the weight of the disk to counteract the effect of the igniting spark.

Before any significance could be attached to the time interval between the two spark records obtained on the smoked strip, it was necessary to measure the time lag in the operation of the coil *j* controlled by the contact breaker disk. This was found to be negligible. The time taken for the pressure pulse to travel from the region of the igniting spark to the disk (a distance of 1.5 inches) was also negligible.

Using a mixture containing 25 per cent. of coal gas (Birmingham), the time interval between the two recording sparks was found to be 0.0005 sec.

The next step in the investigation was to obtain a normal pressure-time diagram with the same gas mixture. A small explosion chamber was fitted with an indicator of the diaphragm type and with an igniting spark gap situated 2 inches away from the diaphragm; it was not possible in the second explosion apparatus to arrange the spark gap at the same distance from the diaphragm as that separating the spark gap and disk in the first experiments, but the effect due to the difference of 0.5 inch is negligible. By arranging a recording spark gap in series with the igniting gap, a record of the passage of the igniting spark was obtained. The result is shown in Fig. 1, the duration of the pre-pressure interval being 0.004 sec.

Comparing the results of the two experiments, it will be seen

that 87.5 per cent. of the pre-pressure interval in the pressure-time diagram is due to lack of sensitiveness in the indicator. Bearing in mind that the contact breaker disk in the first experiment had to be arranged to exert sufficient pressure to resist the pressure pulse due to the igniting spark, it is reasonable to conclude that the pre-pressure interval shown in Fig. 1 is mainly an indicator effect. It follows that the true origin of the pressure curve is separated from the instant of passage of the igniting spark by an interval not greater than that required for a pressure pulse to travel from the region of the spark to the indicator.

THE MARKS AND CLERK LABORATORY,
BIRMINGHAM.

[Received, April 27th, 1923.]

CIII.—*Substitution in the Pyrazole Series. Halogen Derivatives of 3:5-Dimethylpyrazole.*

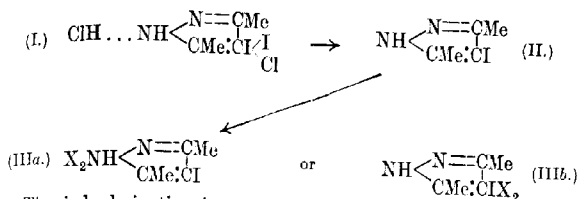
By GILBERT T. MORGAN and ISIDORE ACKERMAN.

THE amino-derivatives of the pyrazole series resemble aromatic amines in regard to the diazo-reaction, and an earlier investigation has demonstrated the exceptionally stable character of the diazonium salts from 4-amino-3:5-dimethylpyrazole (Morgan and Reilly, T., 1914, 105, 430). An attempt has now been made to employ these diazo-derivatives as synthetic agents in the production of substitution derivatives of 3:5-dimethylpyrazole. The results, however, are disappointing, for although iodine can be introduced into the pyrazole nucleus through the agency of diazonium salts the yield of 4-iodo-3:5-dimethylpyrazole is much less than by direct iodination.

3:5-Dimethylpyrazole-4-sulphonic acid is readily produced by direct sulphonation, whereas the Gattermann diazo-process does not lead to a smooth replacement of the diazonium complex by a sulphinic radicle.

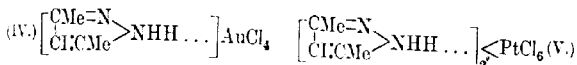
The halogen substitution products of 3:5-dimethylpyrazole are obtained with remarkable facility by direct halogenation.

Iodination occurs much more readily than in the benzene series, for when 3:5-dimethylpyrazole hydrochloride is treated with iodine chloride hydrochloride the initial product is 4-iodo-3:5-dimethylpyrazole iodochloride hydrochloride (I), a very reactive compound which, easily losing its addenda, passes into 4-iodo-3:5-dimethylpyrazole (II), a substance which is also obtained directly from 3:5-dimethylpyrazole in quantitative yield by the action of aqueous potassium periodide in the presence of sodium acetate.

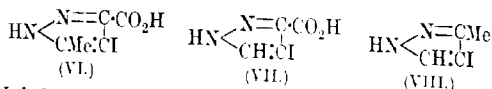


The iodo-derivative is a highly reactive compound yielding a *dichloride* or *dibromide* (formula IIIa or IIIb, where X = Cl or Br). Owing to the two foci of unsaturation, the iodine atom and the imino-group, it is impossible to decide with certainty between the two formulae for these additive products. All attempts to convert the iodo-dichloride into iodoso- and iodoxy-derivatives failed, and consequently it was not found possible to obtain iodonium bases of the pyrazole series.

4-Iodo-3 : 5-dimethylpyrazole (II) has distinctly basic properties, for it can be acylated giving the *acetyl* or *benzoyl* derivative, and it yields such characteristic double salts as the *chloraurate* (IV) and *chloroplatinate* (V).



During various attempts made to prepare iodoxydimethylpyrazole by oxidising the iodine substituent in 4-iodo-3 : 5-dimethylpyrazole, it was noticed that the methyl groups were first attacked, the iodine being left unchanged. The following oxidation products were identified :



4-Iodo-3-methylpyrazole-5-carboxylic acid (VI) is obtained with neutral permanganate whereas 4-iodopyrazole-3 or 5-carboxylic acid (VII) and 4-iodo-3-methylpyrazole (VIII) are produced with alkaline permanganate, their formation being due to a complete removal by oxidation of one methyl group (compare Knorr, *Annalen*, 1894, 279, 218; Marchetti, *Gazzetta*, 1892, 22, [ii], 363; Rottenberg, *Ber.*, 1894, 27, 1097).

Chlorination and bromination of 3 : 5-dimethylpyrazole take place quite readily in aqueous solution.

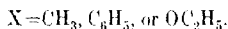
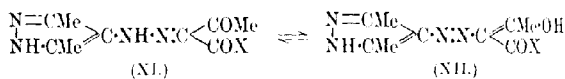


It is noteworthy that 4-bromo-3 : 5-dimethylpyrazole (X) retains the basic properties of the unsubstituted pyrazole; it yields an

acetyl and a benzoyl derivative and forms well-defined, crystalline salts, such as the *hydrobromide* and *chloroaurate*. An orange *perbromide* (IX) is produced when bromine is added to 3 : 5-di-methylpyrazole, dissolved in hydrochloric acid. The constitution of this substance is, however, open to the same uncertainty as that indicated in the case of the dichloride and dibromide of 4-iodo-3 : 5-dimethylpyrazole, but the evidence is rather in support of the view that the active bromine is associated with nitrogen rather than with the bromo-substituent. Similar perbromides have already been noticed in the pyrazole series (Sjollema, *Annalen*, 1894, 279, 248) and among tetrahydronaphthalene derivatives (Morgan, Micklethwait, and Winfield, T., 1904, 85, 736).

3 : 5-Dimethylpyrazole-4-azo- β -diketones.

In studying the reactions of 3 : 5-dimethylpyrazole-4-diazonium chloride it was found that this non-aromatic diazo-derivative would couple with those β -diketones and β -keto-esters which contain potentially the group $\text{CO}\cdot\text{CH}_2\cdot\text{CO}$, but would not condense with those substituted β -diketones and β -keto-esters containing the group $\text{CO}\cdot\text{CHX}\cdot\text{CO}$. This result suggests that the condensation products are tautomeric substances having the hydrazone structure (XI), whereas in alkaline solution they have an enolic constitution, yielding red sodium salts and developing intense red colorations with ferric chloride.



Recent researches on the β -diketones (this vol., p. 445) indicate, however, that in certain conditions enolisation may occur by migration of hydrogen from a terminal methyl group, and in this contingency the development of enolic properties would not be an indication of the presence of the azo-phase (XII).

EXPERIMENTAL.

4-Amino-3 : 5-dimethylpyrazole.

3 : 5-Dimethylpyrazole (m. p. 106.5°), the starting point in this research, was prepared from acetylacetone and hydrazine sulphate by Rosengarten's method (*Annalen*, 1894, 279, 237), the yield with purified reagents being theoretical. The nitration of 3 : 5-dimethylpyrazole formerly carried out with fuming nitric acid (Morgan and Reilly, T., 1914, 105, 430) often proved to be uncontrollable, leading to tarry products; it was improved by using the process adopted

in preparing 4-nitro-3:5-dimethylisooxazole (Morgan and Burgess, T., 1921, **119**, 699). Six c.c. of nitric acid (*d* 1.42) were slowly added at 0° to 10 c.c. of sulphuric acid (*d* 1.84) containing 5 grams of dissolved 3:5-dimethylpyrazole, when the colour of the solution changed from intense to light yellow; a further 20 c.c. of concentrated sulphuric acid were added, the mixture was left over-night and heated on the water-bath for three to four hours until red fumes were no longer evolved. The nitration mixture, poured on to ice, was either extracted repeatedly with ether to remove the dissolved nitro-compound or the latter was precipitated in colourless needles on neutralising the acid with sodium hydroxide. The ethereal extract also yielded these needles, which, after recrystallisation from water, melted at 126°. The yield by either procedure was practically quantitative and the cheaper precipitation by alkali was generally employed.

The foregoing nitro-compound was reduced to 4-amino-3:5-dimethylpyrazole dihydrochloride by tin and hydrochloric acid (Morgan and Reilly, *loc. cit.*), the yield being 77 per cent. of the calculated amount, but a quicker method of obtaining the free base in 85 per cent. yield was achieved by the process used in the preparation of 4-amino-3:5-dimethylisooxazole (Morgan and Burgess, *loc. cit.*). Seven grams of the nitro-compound, dissolved in 100 c.c. of moist ether, were reduced completely by adding a large excess of amalgamated aluminium foil. A vigorous reaction ensued, the containing flask being cooled; the solvent was subsequently distilled off and the residue of amine and aluminium hydroxide extracted with boiling alcohol, 4-amino-3:5-dimethylpyrazole crystallising in colourless prisms from the concentrated extract. This base was characterised by its condensation products with aromatic aldehydes prepared by the same general method of heating the generators in dilute alcohol under reflux. These Schiff bases were soluble in organic solvents excepting light petroleum.

Schiff base.	Appearance.	M. p.
<i>Benzylidene-4-amino-3:5-dimethylpyrazole.</i> [Found: N = 21.25. Calc., 21.10 per cent.]	Colourless needles.	139–140°.
<i>o-Nitrobenzylidene-4-amino-3:5-dimethylpyrazole.</i> [Found: N = 23.00. Calc., 22.95 per cent.]	Greenish-yellow needles, becoming reddish-brown on exposure to light and air.	104°.
<i>m-Nitrobenzylidene-4-amino-3:5-dimethylpyrazole.</i> [Found: N = 23.11 per cent.]	Light yellow needles.	236°.
<i>p-Nitrobenzylidene-4-amino-3:5-dimethylpyrazole.</i> [Found: N = 23.15 per cent.]	Golden-yellow needles.	198°.

The condensation between 4-amino-3:5-dimethylpyrazole and aqueous formaldehyde led to a more complex product which separated as a white powder insoluble in all organic solvents, charring gradually on heating but with no definite melting point below 300° (Found: N = 27.54. $\left[\text{HO-CH}_2\text{-N} \begin{array}{c} \text{N}=\text{CMe} \\ \text{CMe} \cdot \text{C} \cdot \text{N} \cdot \text{CH}_2 \end{array} \right]_x$ requires N = 27.45 per cent.).

Reactions of 3:5-Dimethylpyrazole-4-diazonium Chloride.

All attempts failed to condense the exceptionally stable 3:5-dimethylpyrazole-4-diazonium chloride (Morgan and Reilly, *loc. cit.*) with 4-amino-3:5-dimethylpyrazole; the expected diazoamine was not obtained even on varying considerably the experimental conditions. In the presence of aqueous sodium acetate this diazonium chloride coupled readily, however, with β -diketones and β -keto-esters containing the group $\text{CO-CH}_2\text{-CO}$, but condensation did not occur with methylacetylacetone. The presence of two mobile hydrogen atoms appeared to be an essential condition for this reaction.

Azo-derivative.	Appearance.	M. p.
3:5-Dimethylpyrazole-4-azoacetylacetone. [Found: N = 25.45. Calc., N = 25.23 per cent.]	Golden-yellow needles.	184° (decomposition).
3:5-Dimethylpyrazole-4-azobenzoyleacetone. [Found: N = 19.85. Calc., N = 19.72 per cent.]	Light yellow needles.	169–170° (decomposition).
Ethyl 3:5-dimethylpyrazole-4-azoaceto- acetate. [Found: N = 22.51. Calc., N = 22.22 per cent.]	Orange-yellow crystals.	157°.

These azo-derivatives gave red sodium salts which developed intense red colorations with ferric chloride, thus indicating the azo-enolic structure in alkaline solution.

4-Iodo-3:5-dimethylpyrazole.

1. From 4-Amino-3:5-dimethylpyrazole.—A solution of 3:5-dimethylpyrazole-4-diazonium chloride prepared from 5 grams of 4-amino-3:5-dimethylpyrazole dihydrochloride, 5 c.c. of concentrated hydrochloric acid, 17 c.c. of water, and 2.1 grams of sodium nitrite was added to a boiling solution of 35 grams of potassium iodide in 50 c.c. of water, the mixture being warmed at 100° under reflux until nitrogen was no longer evolved. The solution, now containing a black oil, was made alkaline with sodium hydroxide, when a thick, white precipitate separated. The oil solidified on cooling; the total precipitate was shaken with sodium thiosulphate to remove iodine and dissolved in hot aqueous alcohol, this operation

being repeated until 4-iodo-3:5-dimethylpyrazole separated as an asbestos-like mass of flattened, feathery needles melting at 137°. This iodo-compound, which had a characteristic persistent odour resembling that of the halogenated phenols, was very insoluble in cold but more soluble in hot water; it was dissolved by ordinary organic solvents, appreciably volatile in steam, and revealed a basic character by its ready solubility in aqueous acids (Found: N = 12.67; I = 57.37. $C_5H_7N_2I$ requires N = 12.61; I = 57.20 per cent.).

By the diazo-reaction the yield of this iodo-compound was never more than 60 per cent. of the calculated quantity and the product was difficult to purify.

2. From 3:5-Dimethylpyrazole.—A solution of 15 grams of iodine in concentrated aqueous potassium iodide was added to a boiling mixture of three grams of 3:5-dimethylpyrazole, 5 grams of sodium acetate, and 20 c.c. of water heated under reflux. The liquid assumed a faint yellow colour and a colourless oil separated. On cooling, the oil solidified and the solution became filled with a crystalline precipitate of the iodo-derivative, which after one crystallisation from alcohol melted at 137°, the yield being quantitative (compare Bougault, *J. Pharm.*, 1900, [vi], 11, 100).

Another method for the direct introduction of iodine into 3:5-dimethylpyrazole is described on p. 1315.

Acetyl-4-iodo-3:5-dimethylpyrazole, obtained by mixing the iodo-compound with cold acetic anhydride, crystallised from dilute alcohol in colourless, prismatic crystals melting at 62.5–63.5°. This acetyl compound, which was insoluble in water, dissolved in ordinary organic solvents (Found: N = 11.03; I = 48.6. $C_7H_9ON_2I$ requires N = 10.61; I = 48.10 per cent.).

Benzoyl-4-iodo-3:5-dimethylpyrazole, produced by mixing molecular proportions of benzoyl chloride and the iodopyrazole in ethereal solution, was deposited as a colourless, crystalline precipitate separating from alcohol in clusters of feathery needles melting at 82° (Found: N = 8.65; I = 39.20. $C_{12}H_{11}ON_2I$ requires N = 8.59; I = 38.95 per cent.). The two foregoing acyl derivatives have characteristic odours.

4-Iodo-3:5-dimethylpyrazole chloraurate (formula IV), an orange-yellow, crystalline precipitate obtained from the iodo-compound and auric chloride in hydrochloric acid, melted at 174° (Found: Au = 34.89. $C_5H_7N_2I, H.AuCl_4$ requires Au = 35.05 per cent.).

4-Iodo-3:5-dimethylpyrazole chloroplatinate (formula V), a light orange-coloured, crystalline precipitate melting at 215–220°, contained Pt = 22.78 [$(C_5H_7N_2I)_2.H_2PtCl_6$ requires Pt = 22.83 per cent.]. The foregoing complex salts, although sparingly soluble in water, dissolved readily in alcohol.

Additive Compounds of 4-Iodo-3:5-dimethylpyrazole.

1. *4-Iodo-3:5-dimethylpyrazole Dichloride* (Formula IIIa or b).—Dry chlorine was passed into a cooled chloroform solution (1 in 6) of the iodopyrazole until the solution assumed a yellow colour and solidified to a mass of yellow needles of the dichloride melting at 85–88° with previous softening. The product was very volatile at the ordinary temperature, the vapour being lachrymatory. The active chlorine present was estimated by liberation of iodine from potassium iodide. The results obtained with freshly prepared specimens were high, indicating a further addition of chlorine to the imino-group (Found: after two to three hours on a porous plate, Cl = 24.90, 24.88. $C_5H_7N_2ICl_2$ requires Cl = 24.23 per cent.).

The action of dilute aqueous sodium hydroxide on the dichloride was complicated and destructive and nothing corresponding with the aromatic iodoso-derivatives was isolated. The direct oxidation of 4-iodo-3:5-dimethylpyrazole to an iodoxy-derivative by Caro's acid, acidified permanganate, or bleaching powder was attempted, but without success; the iodo-compound either remained unchanged or was destroyed completely.

4-Iodo-3:5-dimethylpyrazole Dibromide (Formula IIIa or b).—On adding successively bromine (1 mol.) and light petroleum to a chloroform solution of the iodo-compound (1 mol.), a precipitate consisting of brick-red needles was deposited. The product was volatile and lachrymatory and melted indefinitely at 78–81° to a deep viscid liquid; it liberated iodine from potassium iodide and was decomposed by moisture or cold alcohol (Found: Br = 40.48, 40.84; N = 7.51. $C_5H_7N_2IBr_2$ requires Br = 41.86; N = 7.34 per cent.).

4-Iodo-3:5-dimethylpyrazole Iodochloride Hydrochloride (Formula I).—A solution of iodine chloride hydrochloride (Schützenberger, *Compt. rend.*, 1877, **84**, 389) was prepared by boiling under reflux 5 grams of sodium nitrite, 5 grams of potassium iodide, and 20 c.c. of concentrated hydrochloric acid until red fumes ceased to be evolved. The brown solution was extracted with ether and the solvent removed, leaving an orange-red liquid, containing ICl_2HCl , which was slowly added to 3 grams of 3:5-dimethylpyrazole in 10 c.c. of concentrated hydrochloric acid. The colour of the solution disappeared and a voluminous precipitate of yellow plates separated, melting sharply at 111° with frothing (Found: N = 6.72; active Cl = 7.56, 7.64; active I = 27.03, 27.32. $C_5H_8N_2ICl$ requires N = 6.65; active Cl = 8.43; active I = 30.16 per cent.). The iodochloride hydrochloride was an unstable, very reactive substance hydrolysed by water, liberating iodine from potassium

iodide solution, and decomposing aqueous sodium thiosulphate with liberation of sulphur. It gave with starch the characteristic blue colour, and was converted quantitatively into 4-iodo-3:5-dimethylpyrazole (m. p. 137°) by the action of 10 per cent. aqueous sodium hydroxide, so that this decomposition gave a third method for preparing the iodo-derivative.

When dissolved in cold alcohol containing a little water, the iodochloride hydrochloride changed slowly into 4-iodo-3:5-dimethylpyrazole hydrochloride, which separated in long, colourless needles melting at 196° (Found: N = 10.81; I + Cl = 62.96. $C_5H_7N_2I \cdot HCl$ requires N = 10.83; I + Cl = 62.85 per cent.).

Oxidation of 4-Iodo-3:5-dimethylpyrazole.

Three grams of the iodo-compound were added to 4.3 grams of potassium permanganate and 5 grams of potassium hydroxide dissolved in 50 c.c. of water. Oxidation occurred even in the cold and the solution was completely decolorised on boiling. The filtrate from hydrated manganese oxides was acidified, when greyish-white 4-iodopyrazolecarboxylic acid (formula VII) was precipitated. This acid was odourless, amorphous, and insoluble in water or alcohol; it dissolved readily in alkalis. The melting point was indefinite from 70° onwards, the substance decomposing with frothing (Found: N = 11.90; I = 52.91. $C_4H_3O_2N_2I$ requires N = 11.77; I = 53.35 per cent.).

The silver salt, $C_4H_2O_2N_2I \cdot Ag$, a white precipitate from silver nitrate and the acid in ammoniacal solution, gave Ag = 31.01 (Calc., Ag = 31.30 per cent.).

4-Iodo-3-(or 5-)methylpyrazole (formula VIII) a colourless base, was extracted by alcohol from the manganese oxide precipitate accompanied by a small amount of the unaltered 4-iodo-3:5-dimethylpyrazole. The mixed bases were dissolved in concentrated hydrochloric acid and the solution was diluted with water, when 4-iodo-3-(or 5-)methylpyrazole was deposited; the higher homologue remaining in the filtrate was afterwards precipitated by alkalis.

4-Iodo-3-(or 5-)methylpyrazole was redissolved in hydrochloric acid and reprecipitated by water and finally crystallised from dilute alcohol; it separated in colourless needles and melted at 185–187° (Found: N = 13.42; I = 60.95. $C_4H_5N_2I$ requires N = 13.46; I = 61.05 per cent.).

The chloraurate and chloroplatinate were orange-yellow, crystalline precipitates resembling the corresponding salts of 4-iodo-3:5-dimethylpyrazole [Found: Au = 35.52. $C_4H_5N_2I \cdot H \cdot AuCl_4$ requires Au = 35.95 per cent. Found: Pt = 23.31. $(C_4H_5N_2I)_2 \cdot H_2PtCl_6$ requires Pt = 23.60 per cent.].

4-Iodo-3-(or 5-)methylpyrazolecarboxylic acid (formula VI), an amorphous, white substance melting at 237° , insoluble in water or alcohol, was produced by adding 3 grams of 4-iodo-3 : 5-dimethylpyrazole to 9 grams of potassium permanganate in 60 c.c. of water; the colour rapidly disappeared, carbon dioxide was evolved, and the decoloration was completed by warming at 100° for an hour. Acidification of the filtrate led to precipitation of the carboxylic acid (Found : N = 11.10; I = 50.53. $C_5H_3O_2N_2I$ requires N = 11.11; I = 50.40 per cent.).

The white *silver* salt precipitated from ammoniacal solution gave Ag = 30.12 ($C_5H_4O_2N_2IAg$ requires Ag = 30.08 per cent.).

4-Bromo-3 : 5-dimethylpyrazole (Formula X).—Bromine (1 mol.) was added slowly to 2.5 grams of 3 : 5-dimethylpyrazole and 5 grams of sodium acetate in 50 c.c. of cold water and the solution then heated to boiling. An oil separated and solidified on cooling; and after crystallisation from dilute alcohol the bromo-derivative separated in flattened, colourless needles melting at 118° (Found : N = 16.46; Br = 45.42. $C_5H_7N_2Br$ requires N = 16.02; Br = 45.68 per cent.).

4-Bromo-3 : 5-dimethylpyrazole had a pleasant odour less persistent than that of the iodo-derivative; it dissolved in hot water or in the ordinary organic solvents. It had basic properties, yielding salts and acyl derivatives.

The *chloraurate*, an orange-red, crystalline salt, softened at 105° and melted at 126 – 128° (Found : Au = 38.33. $C_5H_7N_2BrHAuCl_4$ requires Au = 38.25 per cent.). This salt is more soluble than the corresponding salt from iododimethylpyrazole, and the chloroplatinate is even more soluble.

1-Acetyl-3 : 5-dimethylpyrazole separated from dilute alcohol in colourless crystals melting at 38° (Found : N = 12.90; Br = 36.71. $C_7H_9ON_2Br$ requires N = 12.91; Br = 36.86 per cent.). The *benzoyl* derivative, obtained by the method employed in benzoylating iododimethylpyrazole, crystallised from alcohol in clusters of flattened needles melting at 48 – 49° (Found : N = 10.16; Br = 28.49. $C_{12}H_{11}ON_2Br$ requires N = 10.03; Br = 28.67 per cent.).

On adding bromine to a solution of 3 : 5-dimethylpyrazole in concentrated hydrochloric acid, the halogen was at first absorbed and then a well-defined, orange-red, crystalline compound separated which proved to be so reactive that it could only be recrystallised from a mixture of chloroform and light petroleum; it was thus obtained in orange-red, hygroscopic needles melting at 142 – 144° (Found : N = 8.63; Br = 71.27. $C_5H_7N_2Br_3$ requires N = 8.34; Br = 71.63 per cent.). The substance liberated iodine from potass-

ium iodide, the amount corresponding with 30.9 per cent. of active bromine.

This perbromide dissolved in alcohol to an orange solution which on warming became decolorised, evolved acetaldehyde, and yielded colourless, acicular crystals of 4-bromo-3:5-dimethylpyrazole hydrobromide melting at 174° . The hydrobromide was also produced on dissolving the orange compound in warm benzene. When added to cold water, the orange compound was transformed into a red oil with liberation of bromine. On warming the mixture, the oil dissolved, the yellow solution rapidly became colourless, and on cooling 4-bromo-3:5-dimethylpyrazole separated.

With 5 per cent. aqueous sodium hydroxide the orange compound changed successively to a pasty red solid and then into the colourless bromodimethylpyrazole.

4-Bromo-3:5-dimethylpyrazole hydrobromide, obtained from the orange perbromide in several of the foregoing reactions in colourless needles (m. p. 174°), had a pungent aromatic odour and dissolved in water to an acid solution (Found: N = 11.23; Br ion = 31.01; total Br = 62.18. $C_5H_7N_2Br \cdot HBr$ requires N = 10.95; Br = 31.23 and 62.47 per cent.).

4-Chloro-3:5-dimethylpyrazole was preferably obtained by passing chlorine into a solution of 2 grams of the pyrazole in 200 c.c. of water. An oily product separated which was extracted with chloroform. The oily residue from this solvent solidified rapidly and after one crystallisation from alcohol melted at 95° (Found: N = 21.51; Cl = 27.19. $C_5H_7N_2Cl$ requires N = 21.46; Cl = 27.20 per cent.).

4-Chloro-3:5-dimethylpyrazole was less basic than the corresponding bromo- and iodo-derivatives. It did not react with acetic anhydride or benzoyl chloride and gave no sparingly soluble chloroaurate or chloroplatinate.

3:5-Dimethylpyrazole-4-sulphonic Acid.—The crystalline form of the barium salt of this acid has been studied by Zschimmer (*Z. Krist. Min.*, 1898, **29**, 231), but this reference has no mention of the preparation of the acid.

Three grams of 3:5-dimethylpyrazole, dissolved in 10 c.c. of fuming sulphuric acid (20 per cent. SO_3), were warmed for six hours on the water-bath. The cooled solution, diluted with water and neutralised with barium carbonate, was filtered and concentrated, when tabular crystals of the barium salt were deposited [Found: Ba = 27.91. $(C_5H_7N_2SO_3)_2Ba$ requires Ba = 28.13 per cent.]. The calculated quantity of dilute sulphuric acid was added to a boiling solution of the barium salt and the filtrate concentrated until 3:5 dimethylpyrazole-4-sulphonic acid separated. This acid,

which is very soluble in water, crystallised in hygroscopic, flattened needles, turning brown at 200° and melting at $287-288^{\circ}$ (Found: N = 14.07; S = 15.59. $C_5H_7N_2SO_3H \cdot 1\frac{1}{2}H_2O$ requires N = 13.79; S = 15.76 per cent.). The acid was sparingly soluble in boiling alcohol; it lost its water of crystallisation at 115° .

3:5-Dimethylpyrazole-4-sulphonyl chloride, $C_5H_7N_2 \cdot SO_2Cl$, was obtained by the action of phosphorus pentachloride on the dry sulphonic acid or its barium salt. The mixture, added to cold water, gave a colourless solid which, when crystallised from dry ether, separated in clusters of feathery needles melting at 100° (Found: N = 14.31; S = 16.32. Calc., N = 14.40; S = 16.45 per cent.).

The yield of this sulphonyl chloride was poor, only 0.2 gram being obtained from 1 gram of the acid. The foregoing barium salt was distilled with dry potassium ferrocyanide, but the volatile product was 3:5-dimethylpyrazole (m. p. 106.5°) and not the expected nitrile of this substance. This nitrile was not obtainable by the Sandmeyer reaction from the aminopyrazole.

The authors desire to express their thanks to the Advisory Council of the Department of Scientific and Industrial Research for grants which have helped to defray the expenses of this investigation.

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[Received, May 2nd, 1923.]

CLIII.—*The Adsorption of the -B and -C Members of the Radium and Thorium Series by Ferric Hydroxide.*

By JOHN ARNOLD CRANSTON and ROBERT HUTTON.

IN a previous paper on this subject (Cranston and Hutton, T., 1922, **121**, 2843) it has been shown that at a given acidity the atomic ratio thorium-B to thorium-C adsorbed by colloidal ferric hydroxide is greater than the ratio of radium-B to radium-C adsorbed and that this different behaviour is maintained when the adsorption is carried out in a mixed solution of the four radio-elements.

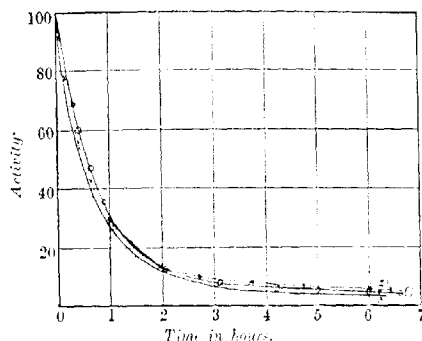
It was to be expected that the initial concentrations of these four substances would be a determining factor in the values of the ratios adsorbed. These initial concentrations were known only approximately in the work previously carried out, and it seemed desirable to perform further experiments in which these concen-

trations were accurately known so that quantitative relationships could be observed to test the colloidal theory put forward.

Accordingly, in the first series of experiments solutions of thorium-B and radium-B were left for four hours and forty-five minutes respectively, to ensure radioactive equilibrium with the -C members.

Series 1.—The procedure was as follows. The active deposit of thorium, obtained in the usual way by exposing a negatively charged platinum plate to thorium hydroxide, was dissolved in 10 c.c. of 0.001*N*-hydrochloric acid, and the solution left for four hours to attain equilibrium. The radium active deposit, obtained by exposing a negatively charged platinum wire to radium emanation, was dissolved in a further 10 c.c. of acid of the same strength

FIG. 1.



and the solution left for forty-five minutes. This operation was carried out so that both solutions attained equilibrium at the same time. The solutions were mixed and the adsorptions carried out by adding 2 c.c. of a colloidal solution of ferric hydroxide (dialysed free from hydrochloric acid). A drop of sodium sulphate was added to precipitate the hydroxide, which was then rapidly filtered and dried, the activity being determined at short intervals in the x-ray electroscope. A decay curve was thus obtained representing the combined effect of the radium and thorium members, and readily capable of analysis so as to give the two ratios Ra-B/Ra-C and Th-B/Th-C (see previous paper). Three decay curves obtained in this way are shown in Fig. 1. They give the following ratios :

	1.	2.	3.
Ra-B/Ra-C adsorbed	0.20	0.18	0.21
Th-B/Th-C adsorbed	2.3	2.2	2.4
Mean ratio Ra-B/Ra-C = 0.20 ... (a_1); mean ratio Th-B/Th-C = 2.3 ... (b_1).			

Before adsorption the substances were present in radioactive equilibrium, that is, $\text{Ra-B/Ra-C} = 1.3 \dots (a_2)$, $\text{Th-B/Th-C} = 10.6 \dots (b_2)$.

Hence, before adsorption $b_2/a_2 = 10.6/1.3 = 8.16$;

after adsorption, $b_1/a_1 = 2.3/0.2 = 11.5$.

Thus it would appear that a partial separation of the isotopic elements Ra-C and Th-C can be obtained by means of adsorption.

It was noted by von Hevesy (*Phil. Mag.*, 1912, [vi], 23, 628) in his investigation of the electrochemical properties of the -B and -C members, by depositing them on metallic electrodes at varying potentials, that radium-C could be separated in a purer state than either thorium-C or actinium-C, that is, less contaminated by the -B member. He concluded that either there are small differences in the electrochemical properties of the three -C members, or that there is a greater probability of some thorium-B separating out with the thorium-C owing to the period of thorium-B being much longer than that of radium-B. A parallelism has already been shown to exist between the electrochemical and adsorptive properties of these elements (Cranston and Burnett, T., 1921, 119, 2036).

Series 2.—It has been found that when an active deposit in which the -B and -C members are in equilibrium is dissolved off a platinum plate or wire by 0.001N-hydrochloric acid, the solution contains a large excess of the -B member over the equilibrium amount. With lapse of time, the ratio of the -C member increases in such a solution until it is in equilibrium with the -B member. By leaving such solutions for different intervals of time, convenient sources of these elements in different relative amounts can be obtained.

The first set of experiments in this series was carried out with radium-B and radium-C. An active deposit was obtained on the platinum wire as before and left for twenty minutes before dissolving in 0.001N-acid, so that the effect of the radium-B would be negligible. In successive experiments, adsorptions with colloidal ferric hydroxide were carried out at varying intervals after dissolving the deposit. The atomic ratio was determined for each experiment from the corresponding decay curve in the manner described in the previous papers, and the following results were obtained:

Time in minutes	3	8	13	15	18	20	25	30	40
Atomic ratio, Ra-B/Ra-C	1.18	0.82	0.62	0.56	0.50	0.45	0.37	0.32	0.22

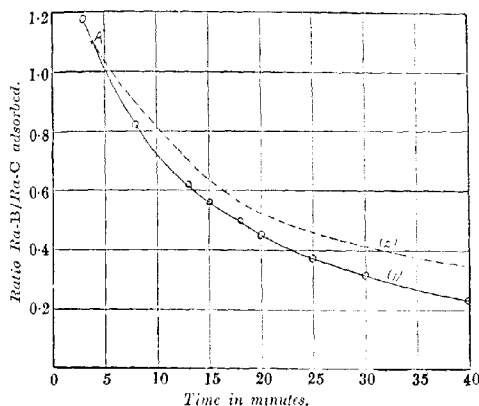
The graph of these results is shown in curve 1, Fig. 2. Curve 2 will be explained later.

The next group of experiments were performed with thorium-*B* and thorium-*C*. An active deposit was obtained on a platinum plate and dissolved off in 0.001N-acid. Adsorptions were carried out as before, but the solutions were left for longer periods after dissolving the deposit. The following ratios were obtained :

Time in hours	0.15	0.35	1.0	2.0	3.0	4.0
Ratio Th- <i>B</i> /Th- <i>C</i> adsorbed	10.3	7.5	3.8	2.9	2.7	2.5

The graph of these results is shown on Fig. 3. It is seen in both cases that with lapse of time there is a regular decrease in the

FIG. 2.



ratio of the -*B* member to the -*C* member adsorbed. It now becomes necessary to determine whether the decrease corresponds with the alteration of the initial relative concentration of these elements in the solution immediately before adsorption. Accordingly, in the next series of experiments on the radium active deposit, a portion of the solution was removed immediately before the adsorption was carried out, rapidly evaporated to dryness, and the ratio Ra-*B*/Ra-*C* determined by the decay curve. Different initial concentrations were obtained in successive experiments by keeping the solutions for various periods after dissolving from the wire.

Series 3.—

Ratio Ra- <i>B</i> /Ra- <i>C</i> present before adsorption	3.25	3.1	2.0	1.8	1.6	1.3
Ratio Ra- <i>B</i> /Ra- <i>C</i> adsorbed	1.15	1.1	0.6	0.55	0.45	0.2

The graph of these results is shown on Fig. 4. It is apparent that the concentration of radium-*B* and of radium-*C* in the solution

immediately before adsorption is not the sole factor in determining the amounts of these elements adsorbed, but that in some way the age of the solution is involved so that the longer the solution has existed the greater the relative amount of the -C member adsorbed. If this time factor were connected in any way with the rate of growth of radium-C and thorium-C, it would not operate

FIG. 3.

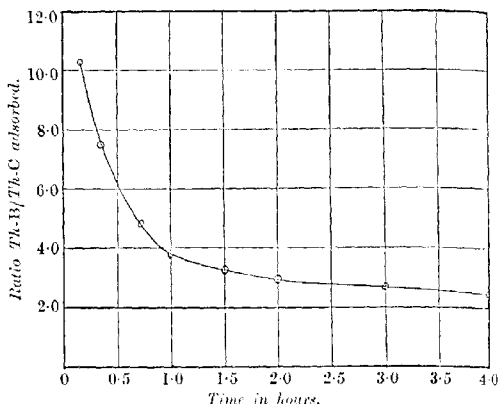
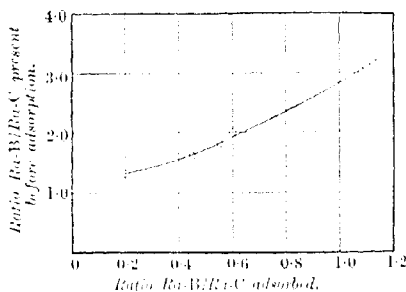


FIG. 4.



equally in the two series, and the different behaviour of these isotopic elements obtained in the experiments of series I would be expected.

An explanation of this phenomenon, put forward in the two previous papers already referred to, may be summarised here as follows. In 0.001N-acid solution a small proportion of the δ

On assumption (ii), the calculated ratio $\text{Ra-B}/\text{Ra-C}$ adsorbed ten minutes after time t is obtained as follows :

As before, the original xP atoms of radium-B decay to $0.77xP$ atoms and give rise to $0.18xP$ atoms of radium-C, all of which are adsorbed. The total radium-C remaining is $0.70Q + 0.18(1 - x)P$, of which the fraction y is adsorbed.

Hence the ratio $\text{Ra-B}/\text{Ra-C}$ adsorbed at the end of ten minutes

$$= 0.77xP / (0.18xP + 0.70yQ + 0.18yP - 0.18xyP),$$

x and y are both experimentally found to be small fractions, approximately 0.05 and 0.12, respectively, so that the term $0.18xyP$ can be neglected.

The ratio $\text{Ra-B}/\text{Ra-C}$ adsorbed then becomes $= 0.58$.

In a similar way, the ratio adsorbed at $t + 20$ minutes can be shown to be

$$= 0.595xP / (0.285xP + 0.49yQ + 0.285yP) = 0.39,$$

and the ratio adsorbed at $t + 30$ minutes can be shown to be

$$= 0.455xP / (0.306xP + 0.35yQ + 0.306yP) = 0.31.$$

The experimental curve of Fig. 2 shows that the ratios $\text{Ra-B}/\text{Ra-C}$ adsorbed at $t + 10$, $t + 20$, $t + 30$, are 0.59, 0.39, and 0.29, respectively, and therefore in close agreement with the above values obtained from the second assumption.

Summary.

1. Previous work on the adsorption of -B and -C members of the radium and thorium series by ferric hydroxide has been continued.

2. Under similar conditions, the ratio of $\text{Th-B}/\text{Th-C}$ adsorbed by ferric hydroxide is greater than the ratio of their isotopes, $\text{Ra-B}/\text{Ra-C}$, even when the initial different relative concentrations of the solutions are taken into account.

3. The interval of time between preparing the solutions and the carrying out of the adsorptions has been found to be an important factor in determining the ratio adsorbed.

4. The influence of this time factor is in quantitative agreement with that expected from the theory put forward to explain the greater proportion of the -C member adsorbed with the lapse of time.

The authors are indebted to The Glasgow and West of Scotland Radium Committee for supplying quantities of radium emanation from which the active deposits were prepared.

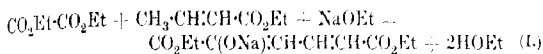
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[Received, April 26th, 1923.]

(CIV.— γ -Oxalyl Derivatives of $\beta\beta$ - and $\alpha\beta$ -Dimethylacrylic Acids.

By LUCY HIGGINBOTHAM and ARTHUR LARWORTH.

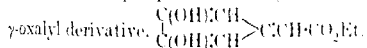
SINCE it was observed by one of us (T., 1901, 79, 1276) that ethyl crotonate is converted into ethyl sodio- γ -oxalylcrotonate by the action of ethyl oxalate in presence of sodium ethoxide in accordance with the equation



no other condensation of precisely this type in the aliphatic series has been described, although Wislicenus and Schöllköpf (*J. pr. Chem.*, 1917, [ii], 95, 269 *et seq.*) record the conversion of ethyl β -ethoxycrotonate, by means of ethyl oxalate and potassium ethoxide, into a cyclic compound which is evidently derived from the γ -oxalyl derivative of the ethoxycrotonate by elimination, at the α -position, of another molecule of alcohol.

In the former of the above papers, it was noted that other aliphatic compounds which, like ethyl crotonate, contain the group $\text{CH}_3\cdot\text{CH}\cdot\text{CH}\cdot\text{CO}$ yield, on treatment with ethyl oxalate and sodium or its alkyl oxides, compounds which resemble the γ -derivative of ethyl crotonate inasmuch as they have acidic properties and give with ferric chloride black colorations contrasting strongly with the red to violet colorations obtained when this reagent is applied to α -oxalyl derivatives of carbonyl compounds.

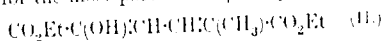
Numerous points of interest in connexion with condensations of the above type, especially in relation to the question of induced latent polarities of atoms in carbon chains, have recently made it desirable to extend the original experiments, and the study of ethyl $\beta\beta$ -dimethylacrylate, $\text{C}(\text{CH}_3)_2\text{CH}\cdot\text{CO}_2\text{Et}$, one of the next higher homologues of ethyl crotonate, was therefore undertaken. This compound was one of those which had previously given evidence of yielding a γ -oxalyl derivative (*loc. cit.*) and it was thought likely to be specially interesting as, in virtue of the fact that it contains two methyl groups, each situated with regard to the carbonyl group precisely as the single methyl group in ethyl crotonate is situated, there was some prospect that it might be convertible into the cyclic



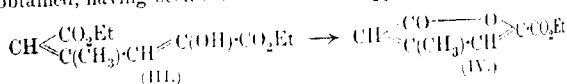
The " $\beta\beta$ -dimethylacrylic ester" used in the opening series of experiments was prepared from a sample of " α -Bromisovaleriansäures VOL. CXXIII.

Aethyl " purchased from Kahlbaum, by heating it with diethylamine and carefully fractionating the neutral product. As the agent for condensing the unsaturated ester with ethyl oxalate, potassium ethoxide was employed and a number of crystalline products of the reaction were ultimately isolated. Extended experiments on these products showed that they fell into two isomeric series, and, whilst the individuals of either series were interconvertible, no representative of the one series could be converted into a representative of the other series. This appeared definitely to exclude the probability that the two series were related stereochemically and aroused the suspicion that the dimethylacrylic ester used was not a homogeneous product. As the original bromo-ester from which it was prepared had probably been made from fusel oil, through the mixture of valeric acids which it affords on oxidation, it seemed likely that the two independent series of compounds under observation were derived from $\beta\beta$ -dimethyl- and $\alpha\beta$ -dimethyl-acrylic acids, respectively. This hypothesis was put to the test by carrying out the whole series of operations, first with an ester made by esterifying pure crystalline $\beta\beta$ -dimethylacrylic acid, when only one of the two series of compounds was produced. The second series was subsequently obtained alone by submitting synthetic ethyl $\alpha\beta$ -dimethylacrylate to the same operations.

There is no doubt that both $\beta\beta$ -dimethylacrylate and $\alpha\beta$ -dimethylacrylate condense with ethyl oxalate in the γ -position. In both cases, the main reaction takes place in the first instance much as in the case of ethyl crotonate (β -methylacrylate), that is, between one molecule of unsaturated ester and one molecule of ethyl oxalate. There is, however, one marked distinction between the γ -oxalyl derivatives of the two isomeric esters which is of considerable interest and which greatly delayed the correct interpretation of the first results obtained by the authors when working with the mixed esters. The distinction is, that in the process of working up the condensation products, those from the $\alpha\beta$ -dimethyl isomeride are secured for the most part as the γ -oxalyl derivative,



but the corresponding derivative (III) of the $\beta\beta$ -dimethyl ester is not obtained, having been converted into the pyrone compound (IV).



The true oxalyl derivative of the $\beta\beta$ -isomeride can, however, be obtained as the free acid (V), $\text{CO}_2\text{H}\cdot\text{C}(\text{OH})(\text{CH}\cdot\text{C}(\text{CH}_3)\text{CH}\cdot\text{CO}_2\text{H})$, by first converting (IV) into the corresponding acid and subsequently

subjecting the latter to treatment with excess of alkali, when the pyrone ring is opened.

It is somewhat remarkable that the presence of a methyl group replacing hydrogen in the β -position in the ethyl γ -oxalocrotonate should so greatly augment the tendency towards the formation of the pyrone ring. Nevertheless it is quite consistent with the well-known depressant effect on the reactivity of carbonyl of substituting groups in the α -position that the α -methyl derivative (V) does not so readily yield a pyrone derivative as the β -methyl derivative does.

Apart from this feature there is little distinction in chemical character to be observed between the γ -oxalyl compounds of crotonic ester and its α - and β -methyl derivatives. The γ -oxalyl derivative (II) yields the corresponding acid on hydrolysis with alkalis, and both this and the ester itself, when heated with concentrated hydrochloric acid, are converted into the hydroxypyronecarboxylic acid (VI), $\text{CMe} \begin{smallmatrix} \diagup \text{CO} - \text{O} \\ \diagdown \text{CH} - \text{CH} \end{smallmatrix} \text{C} \cdot \text{CO}_2\text{H}$, the ester of which is isomeric with (IV). This acid and its ester are reconverted by alkalis into the free dicarboxylic acid corresponding with (II).

EXPERIMENTAL.

Section I. Preparation and Properties of Derivatives of γ -Oxalyl- $\beta\beta$ -dimethylacrylic Acid.

A description of the earlier experiments on the action of ethyl oxalate on the mixed dimethylacrylic esters made from Kahlbaum's "2-Bromisovaleriansäures Äthyl" need not be given and is dealt with at sufficient length in the introductory section.

(a) *Preparation of the Pure Ethyl $\beta\beta$ -Dimethylacrylate used.*—A lengthy series of experiments was made with the object of testing the numerous alternative methods which are to be found in the literature for the preparation of this ester or the corresponding acid. The inquiry left little doubt that by far the most convenient and economical method is to prepare mesityl oxide from acetone by the process worked out by Conant and Tuttle ("Organic Syntheses," John Wiley and Sons, 1921, p. 53), to oxidise the mesityl oxide by means of sodium or potassium hypochlorite (Barbier and Leser, *Bull. Soc. chim.*, 1905, [iii], **33**, 815) to dimethylacrylic acid, and subsequently to esterify the pure crystalline acid (Perkin, T., 1896, **59**, 1471). The yields are excellent throughout.

(b) *Action of Potassium Ethoxide on a Mixture of Ethyl $\beta\beta$ -Dimethylacrylate and Ethyl Oxalate. Formation of Ethyl 4-Methyl- α -pyrone-6-carboxylate (Formula IV) and 4-Methyl- α -pyrone-6-carboxylic Acid.*—Powdered metallic potassium (4 grams) was

suspended in cold ether (40—100 c.c.) in a flask immersed in a freezing mixture. Anhydrous alcohol (4.7 grams) was added drop by drop over a period of several hours, the whole being allowed to remain over-night, when the conversion of the metal into finely divided ethoxide was complete. After the contents of the flask had again been cooled below 0° , a mixture of ethyl oxalate (7.5 grams) and pure ethyl $\beta\beta$ -dimethylacrylate was very slowly added. The nearly colourless ethoxide dissolved wholly or partly and was finally replaced by a yellow solid, which, after three hours, was separated by filtration and washed with dry ether. The solid was dissolved in cold water and the solution extracted several times with ether to remove neutral impurities. On addition of acetic acid there was no precipitate, the absence of any appreciable quantity of ethyl γ -oxalyl dimethylacrylates thus being demonstrated. On addition of sulphuric acid, however, a solid was deposited in silvery crystals and on extracting the mother-liquor from these with ether a total of 5 grams of the substance was secured. (Such a precipitate is not produced when ethyl α -methylcrotonate is used in place of the β -methylcrotonate.)

This compound, 4-methyl- α -pyrone-6-carboxylic acid, is soluble in hot water, sparingly soluble in cold, and dissolves freely in hot alcohol, but is nearly insoluble in chloroform or benzene. It dissolves in aqueous sodium carbonate, forming a colourless solution from which it is precipitated in hydrated form on addition of mineral acids. It gives no coloration with ferric chloride.

The acid crystallises from water in long, colourless needles which have an indefinite melting point. Heated in a narrow tube, these partly fuse at $97-100^{\circ}$, but do not liquefy completely until 189° ; when allowed to solidify, the mass subsequently melts once more at 194° (Found: C 48.7; H 4.7; H_2O , lost at 120° , = 10.3. $C_7H_6O_4 \cdot H_2O$ requires C 48.8; H 4.7; H_2O 10.5 per cent.).

The equivalent, determined by titration against $N/10$ -sodium hydroxide in the cold, was 173; a monobasic acid, $C_7H_6O_4 \cdot H_2O$, requires 172. After boiling the acid for a minute with excess of the standard alkali, the solution was bright yellow and, on titrating the permanent excess of alkali, the equivalent had apparently sunk to 85.7 (calc. 86), corresponding with the conversion of the acid into the open-chain dicarboxylic acid, γ -oxalyl- $\beta\beta$ -dimethylacrylic acid.

If the above methylpyrone-carboxylic acid is warmed on the water-bath for two hours with excess of 10 per cent. sodium hydroxide, it is converted into a crystalline acid which is readily soluble in water, extracted with difficulty by ether, and melts and decomposes at 220° . The new acid gives no coloration with ferric chloride, dissolves sparingly in chloroform, benzene, or cold water, but

readily in ethyl acetate or alcohol; its equivalent is approximately 77. Possibly this acid corresponds with that obtained by Simonsen from 6-methyl-2-pyrone-3:5-dicarboxylic acid by a similar process (T., 1908, **93**, 1022; 1910, **97**, 1910), in which case it would no doubt be 3:5-dimethylbenzene-1:2:4-tricarboxylic acid (equivalent = 79.3).

The *ethyl* ester, $C_6H_5O_2CO_2Et$, of 4-methyl- α -pyrone-6-carboxylic acid is readily made by esterification of the acid with alcoholic sulphuric acid. It is also formed in small quantity when ethyl $\beta\beta$ -dimethylacrylate is condensed with ethyl oxalate as above described. It is soluble in all the usual organic media with the exception of petroleum and crystallises in long needles melting at 68° (Found: C = 59.1; H = 5.6. $C_9H_{10}O_4$ requires C = 59.3; H = 5.5 per cent.).

The compound gave no coloration with ferric chloride and also gave negative results when attempts were made to convert it into an oxime, semicarbazone, or nitrophenylhydrazone. It was reconverted into the corresponding acid when heated with hydrochloric acid.

γ -Oxalyl- $\beta\beta$ -dimethylacrylic Acid (5-Hydroxy-3-methylmaleonic Acid. Formula V).—This compound may be made by dissolving the preceding methylpyronecarboxylic acid or its ester in excess of cold 30 per cent. sodium hydroxide solution and, after one and a half hours, adding excess of cold hydrochloric acid and extracting with ether. It resembles γ -oxalylcrotonic acid in general properties, dissolves sparingly in cold ether and still more sparingly in benzene or chloroform, but is fairly freely soluble in alcohol and in hot water. It forms small, yellow crystals which melt and decompose at 162 – 163° . Its solutions give intense greenish-black colorations with ferric chloride. The equivalent, determined by titration against sodium hydroxide, was 85.9, whilst a dibasic acid, $C_7H_8O_5$, requires 86.

Heating with hydrochloric acid or acetic anhydride reconverts this compound into 4-methyl- α -pyrone-6-carboxylic acid. It gives no sodium oxalate when boiled with excess of alkali, but is quickly converted into the free acid.

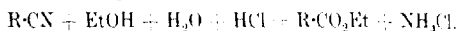
Section II. Preparation and Properties of Derivatives of γ -Oxalyl- $\alpha\beta$ -dimethylacrylic Acid.

After a lengthy examination of methods available for the preparation of pure $\alpha\beta$ -dimethylacrylic ester, the following series of operations was found to yield very satisfactory results.

(a) *Preparation of the Cyanohydrin of Methyl Ethyl Ketone.*—Methyl ethyl ketone (72 grams), made by careful fractional distillation of the commercial mixture passing under this name, was added to a solution of sodium cyanide (98 grams = 2 mols.) in 200 c.c. of water,

contained in a stoppered bottle. Solid sodium hydrogen carbonate (168 grams) was then added gradually, the stopper being replaced after each addition and the whole shaken. The temperature rose gradually, usually about 13° , and as crystals, presumably of hydrated sodium carbonate, separated at one stage, water was added in quantity sufficient to dissolve them. The total time required for the addition was about one and a half hours, and the cyanohydrin then floated as a brown oil. In order to stabilise the product the whole was rendered acid to methyl-orange by addition of hydrochloric acid diluted with water, and the cyanohydrin extracted with ether, the latter then being dried over anhydrous sodium sulphate and evaporated. The residue, after exposure to the temperature of the steam-bath for forty-five minutes, weighed 100 grams, and, by estimation of the amount of cyanide formed by treating a weighed quantity of it with alkali, was found to contain 86 grams of cyanohydrin.*

(b) *Preparation of Ethyl α -Hydroxy- α -methylbutyrate*.—The most effective process of hydrolysis of the cyanohydrin was found to be that based on the equation



The crude cyanohydrin (81 grams) was dissolved in a mixture of alcohol (100 c.c.) and water (15 c.c., = 1 mol.), and dry hydrogen chloride was passed in. The whole increased in weight by 57 grams and after remaining over-night was heated on the steam-bath for three hours. A stream of dry hydrogen chloride was then passed into the boiling solution for another fifteen hours, by which time the hydrolysis was practically complete. (It may prove necessary to remove solid ammonium chloride by filtration at an intermediate stage.) On cooling, pouring into water, and extracting with ether, preferably in a continuous extraction apparatus, a mixture of α -hydroxy- α -methylbutyric acid and its ester was obtained. From this mixture, for example by neutralisation with sodium carbonate, extraction with ether, and fractionation of the extract in a vacuum, at least 58 grams of the ester (b. p. $48-50-65$ mm.) can be obtained (The free acid which is formed in considerable quantities as a secondary product is difficult to extract from its aqueous solutions except by using a continuous extraction apparatus, but may so be isolated and subsequently esterified.)

(c) *Preparation of Ethyl α , γ -Dimethylacrylate*. The preceding hydroxy-ester was converted into the corresponding unsaturated

* As cyanohydrins of ketones under the conditions in which they are formed are largely dissociated into their constituents, a theoretically perfect conversion is not to be anticipated. The above yield, which is 86 per cent. of that theoretically possible, may be considered very satisfactory.

ester by a modification of the method of dehydration first used by Frankland and Duppa (*Annalen*, 1865, **136**, 9).

Phosphorus trichloride (18 grams) was added gradually to cold ethyl α -methyl- α -hydroxybutyrate (30 grams). After about five minutes there was a rise in temperature and hydrogen chloride was evolved. The whole, having subsequently been heated for one and a half hours on the steam-bath, was distilled under atmospheric pressure, and the portion passing over below 154° was washed with water until free from mineral acid, dissolved in ether, dried, and refractionated at 20 mm. pressure. A mixture of unsaturated esters boiling at 54 – 60° was obtained, the yield amounting in all to 80 per cent. of that theoretically possible. The mixture no doubt contained the two stereoisomerides, but, as was expected, it gave only one * oxalyl derivative.

(d) *Condensation of Ethyl $\alpha\beta$ -Dimethylacrylate with Ethyl Oxalate in presence of Potassium Ethoxide.*—If the condensation of ethyl oxalate with either the $\alpha\beta$ -dimethylacrylic ester prepared as above or with that made by removing the elements of hydrogen bromide from Kahlbaum's " α -Bromisovaleriansäures Äthyl" is carried out in the manner described at the beginning of Section (Ib) and the yellow deposit is treated as there described, it is found that addition of acetic acid at the point indicated leads to the formation of a precipitate where none is produced when the starting material is pure $\beta\beta$ -dimethylacrylic ester. This precipitate consists of the following compound in a nearly pure state.

Ethyl γ -Oxalyl- $\alpha\beta$ -dimethylacrylate (Formula II).—This ester is readily soluble in the usual organic media, but is nearly insoluble in water and in light petroleum. It separates from most solvents in colourless prisms which melt at 91 – 92° (Found: C = 57.7; H = 7.0. $C_{11}H_{16}O_5$ requires C = 57.9; H = 7.0 per cent.).

In chemical character it closely resembles ethyl γ -oxalylcrotonate and in alcoholic solution it gives a deep black coloration with ferric chloride. It dissolves in excess of dilute, cold alkali and even in hot sodium carbonate solutions, forming yellow solutions from which acids precipitate it unchanged. Potassium hydroxide solution, if sufficiently strong, converts it into a potassium-derivative, which can be crystallised with some difficulty from alcohol and then appears in bright yellow needles.

γ -Oxalyl- $\alpha\beta$ -dimethylacrylic Acid ($C_9H_{12}O_6$, γ - α -methylgluconic Acid), $CO_2H \cdot C(OH)(CH_3) \cdot CH \cdot CH_2 \cdot C(CH_3)_2 \cdot CO_2H$. This acid is most easily prepared, not directly from the diethyl ester, but from

* Compare T., 1901, **79**, 1272, where the mechanism postulated requires that the sodium derivative of the $\beta\beta$ unsaturated form is what reacts with the ethyl oxalate.

3-methyl- α -pyrone-6-carboxylic acid (formula VI), by heating it on the water-bath with excess of 5 per cent. aqueous sodium hydroxide for half an hour, then cooling, and acidifying with hydrochloric acid. Its properties resemble those of the isomeric acid, but it melts and decomposes at 226° . Like other γ -oxalylacrylic derivatives, it gives in solution deep black colorations with ferric chloride. It was not found easy to prepare quite pure specimens of this acid for analysis; the best sample, when titrated against cold $N/10$ -sodium hydroxide, had the equivalent 87.9, and, after boiling with excess of the alkali and titrating back, had the equivalent 84.4. A monobasic acid, $C_7H_6O_5$, requires 86.

The yellow sodium salt is obtained in crystals by dissolving the corresponding methylpyronecarboxylic acid in hot 30 per cent. sodium hydroxide and allowing to cool.

3-Methyl- α -pyrone-6-carboxylic Acid (Formula VI).—This substance is obtained in a nearly pure form by boiling diethyl γ -oxalyl- $\alpha\beta$ -dimethylacrylate with excess of hydrochloric acid until it is dissolved, and then evaporating to dryness on the water-bath. It is soluble in alcohol, sparingly soluble in ether and in cold water, and separates from hot water, or better from hydrochloric acid, in small needles melting at 246 – 247° . The equivalent, determined by titration of two samples of the acid against $N/10$ -sodium hydroxide, was (a) 154.3 and (b) 154.6. When it was boiled with excess of alkali and the permanent excess of the latter determined by standard acid, the apparent equivalents were (a) 76.5 and (b) 77.1. A monobasic acid, $C_8H_8O_6$, requires 154 and a dibasic acid 77. The crystals of this acid, unlike those of the isomeride, are therefore anhydrous.

The acid gives no coloration with ferric chloride and in other chemical respects closely resembles the isomeric 4-methylpyrone-carboxylic acid (p. 1328).

On esterifying the acid with absolute alcohol containing concentrated sulphuric acid, the *ethyl* ester is obtained. This is insoluble in aqueous sodium carbonate, sparingly soluble in light petroleum, but readily soluble in most of the other common organic media. It crystallises from benzene in diamond-shaped plates melting at 108 – 111° . After distillation in a vacuum, however, the compound melted at 116° .

The authors' thanks are due to the Advisory Council of the Department of Scientific and Industrial Research for a grant to one of us (L. H.) which enabled the work to be done.

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[Received, May 2nd, 1923.]

(LV).—*The Influence of Temperature on Two Alternative Modes of Decomposition of Formic Acid.*

By CYRIL NORMAN HINSHELWOOD and HAROLD HARTLEY.

IN a previous investigation (Hinshelwood, Hartley, and Topley, *Proc. Roy. Soc.*, 1922, [A], **100**, 575) of the alternative reactions by which the thermal decomposition of formic acid vapour may take place in contact with a glass surface, one of the principal experimental results was that the velocity of the reaction yielding carbon dioxide and hydrogen increases with temperature much more rapidly than the alternative reaction in which carbon monoxide and water are produced. A possible interpretation of this result was suggested, and it was shown that the apparent heat of activation of the first reaction is approximately 28,000 calories, and of the second 16,000 calories.*

We have thought it desirable to extend the former observations in certain respects in order to investigate further:

1. The influence of the nature of the glass surface.
2. The effect of increasing the temperature range of the experiments.
3. The proportion of the different products formed at different stages of the decomposition, and their influence on the reaction.

1. *Influence of the Nature of the Glass Surface.*

The velocity of the decomposition and the relative ease with which it follows the two alternative paths are very sensitive to the nature of the glass surface. Tingey and Hinshelwood found that on platinum surfaces the relationships were very different from those observed on glass. Hence a new series of experiments on glass surfaces of a different type was made for the sake of comparison with the original series. The experiments were made in bulbs of Duro glass of the same shape and size, and from the same supply of tubing. The experimental details are described in *Trans.*, 1922, **121**, 1668. Formic acid of 90 per cent. strength was employed. The results are given in Table I. and Fig. 1.

Individual experiments exhibit the large variations which are inevitable in dealing with this subject, but the averages show the

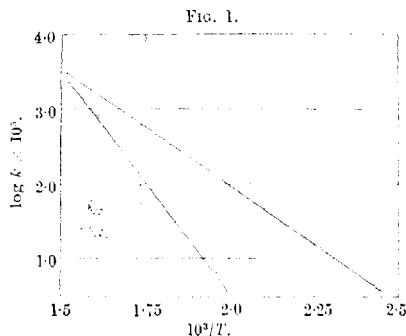
* Adkins and Nissen (*J. Amer. Chem. Soc.*, 1923, **45**, 809) have confirmed the higher temperature coefficient on glass of the reaction yielding carbon dioxide, and state that with alumina the relative size of the temperature coefficients varies with the method of preparation of the alumina.

In a criticism of our interpretation they are mistaken in assuming that the rate was in any way connected with "testing the radiation hypothesis as to the causation of reactions."

TABLE I.

Temperature.	Average value of k_{CO} .	Percentage of $(CO_2 + H_2)$ in product.	Average value of the fraction of formic acid decomposed in the experiments.	Number of experiments.
137.5°	0.000049	1.5	0.24	4
185	0.00036	1.6	0.42	4
236	0.00121	2.5	0.30	3
236	0.00114	9.0	0.28	3
239	0.00144	3.4	0.41	4
302	0.00465	10.8	0.19	5
302	0.0058	14.4	0.30	5
350	0.0159	29.1	0.34	5

Approximate values of k_{CO_2} : at 350°, 0.0065; at 302°, 0.00098 and 0.00056; at 237°, 0.000066.



main regularities surprisingly well. The catalytic activity of the new glass differed rather markedly from that of the glass originally used. This may be seen from a comparison of the percentage of carbon dioxide and hydrogen in the products of complete decomposition at 300°:

Original glass 74%_{CO}, 73%_H, 63%_{CO}.

New glass 19.1%_{CO}, 18.3%_H, 16.5%_{CO}.

These differences are somewhat accentuated by the fact that in the present experiment 90 per cent. formic acid was used whilst in the earlier ones rather weaker acid was used (the effect of this will be explained in a later paragraph). But in spite of the altered conditions, the same influence of temperature on the relative rates of the two reactions is found. This is seen in the figure. In the original experiments the two curves cut at about 280°, while these cut at about 400°. Nevertheless, the regularity on which we have laid most stress—the relative positions of the two curves—is reproduced.

2. *The Effect of Increasing the Temperature Range.*

It was sought if possible to extend the measurements over a wider range of temperature, in order to ascertain whether the apparent heat of activation could be regarded as a constant quantity, and in particular whether its value for the reaction yielding carbon monoxide would retain the same low value at temperatures where this reaction is the only one occurring to an appreciable extent.

Considering the experimental difficulties, it will be seen that when the values of k_{co} are plotted against $1/T$ there are no deviations from the linear relation of much significance. The range of temperature is from 138° to 350° , that is, more than 200° , compared with the previous range of from 240° to 300° . At the lower temperatures, the proportions of carbon dioxide and hydrogen produced are too small to allow the accurate determination of the temperature coefficient of k_{co_2} . The values of k_{co_2} are also inaccurate for another reason, which will be explained shortly.

The values of the heat of activation calculated from the curves in the figure are

$$E_{\text{co}} = 12,000 \text{ calories approximately.}$$

$$E_{\text{co}_2} = 24,500 \text{ calories approximately.}$$

In the original series, these values were about 16,000 and 28,000 calories, respectively, so that the same relation between the two is preserved.

3. *The Proportion of Different Products Formed at Different Stages of the Decomposition.*

Our attention was directed to a discussion of heterogeneous catalysis by Bancroft (*J. Physical Chem.*, 1917, **21**, 573), in which he quotes an observation of Berthelot on the products of decomposition of formic acid, who found in two isolated experiments that when a third of the formic acid was decomposed the reaction appeared to be $\text{HCO}\cdot\text{OH} \rightarrow \text{CO} + \text{H}_2\text{O}$, whilst complete decomposition appeared to correspond to $2\text{HCO}\cdot\text{OH} \rightarrow \text{H}_2\text{O} + \text{CO} + \text{CO}_2 + \text{H}_2$.

Bancroft takes the observations to mean that the initial production of carbon monoxide and water hinders the further progress of the reaction along this path. The matter required further investigation, because if the proportions of the products of the reaction change greatly during its course the quantitative values obtained for the temperature coefficients would be affected, though the fact that k_{co_2} is much more influenced by temperature than k_{co} would remain, since it was based upon analysis of the products of complete decomposition.

Table II shows the results of a number of experiments made to test the point.

TABLE II.

Series.	Temperature.	Time in minutes.	Fraction decomposed.	Percentage of CO ₂ .
1	300°	42	0.187	11.1
		45	0.213	16.4
		90	0.352	19.0
		115	0.42	18.4
		200	0.633	19.6
2	304	240		16.5
	304	250		18.3
	304	365		19.1
	304	365		18.3
3	300	45	0.300	9.9
		45	0.270	19.5
		90	0.503	16.9
		120	0.725	19.6
		150	0.648	17.5
4	239	420		5.6
	259	1440		6.8
5	297	19	0.059	19.2
	299	10	0.046	26.1
	297	40	0.160	19.6
	297	80	0.370	15.0
6	341	5	0.069	48.6
	342	10	0.144	27.8
	342	10	" "	19.0
	342	15	" "	26.6
	342	50	" "	33.5
7	342	70	" "	63.0
	345	10	0.214	59.4
	345	40	0.85	74.0
	345	65	" "	74.1
8	286	20	0.086	27.0
	285.5	50	0.151	18.7
	287	120	0.31	14.6
	(Irregular)	210	0.57	27.2
	285	260	0.46	16.7
9	283	475	0.72	42.1
	344	10	0.32	35.6
	344	20	0.53	50.4
	344	60	0.7	51.3

Series 1-6, Duro glass.

Series 7-9, Soda glass.

In series 1, 2, and 3, which are the most regular, there is some rise in the proportion of carbon dioxide at first, but not to an extent which would modify appreciably the values of the temperature coefficients. We may also cite the complete analogy between the original results, where the analyses were made on the completely decomposed products, and the new results in Table I, where the analyses were made after the decomposition had proceeded to about one-third of the whole way, to show that the former conclusions about the influence of temperature need no modification.

If the reaction yielding carbon monoxide is hindered by the accumulation of its products to such an extent that the rival reaction after a time overtakes it and predominates, as Bancroft suggests, then, either the products of the reaction must poison the catalyst by occupying a large proportion of its surface, or the reverse reaction $\text{H}_2\text{O} + \text{CO} \rightleftharpoons \text{HCO}\cdot\text{OH}$ must attain on the catalyst a speed of the same order as that of the direct reaction. This second possibility cannot be entertained, because the alternative path of decomposition is open all the time to the formic acid so produced, with the result that a continuous transformation of carbon monoxide and water into carbon dioxide and hydrogen should take place. In other words, the catalyst should be capable of bringing about the water-gas reaction at a speed commensurate with that of the formic acid decomposition, which certainly does not occur. It seems, then, that the mode of decomposition of the adsorbed formic acid is conditioned by independent probabilities and not determined to any appreciable extent by the equilibria $\text{H}_2\text{O} + \text{CO} \rightleftharpoons \text{HCO}\cdot\text{OH}$ and $\text{H}_2 + \text{CO}_2 \rightleftharpoons \text{HCO}\cdot\text{OH}$.

A further ground for belief in the complete independence of the two reactions is the fact that the carbon monoxide reaction has the same low temperature coefficient when it is the only reaction, proceeding with appreciable velocity, as it has when the alternative reaction accounts for a large proportion of the products, that is to say, where its low temperature coefficient might have been explained by the assumption that the rate of production of carbon dioxide was increasing at the expense of the monoxide.

With regard to a poisoning action of carbon monoxide, it would seem that if it reduces the velocity of one reaction by covering the surface of the catalyst, it should also reduce that of the other reaction to the same extent. But there is no indication from velocity measurements that the products of the reaction yielding carbon monoxide exert any retarding influence. The following figures, obtained at 210°, where the products were almost exclusively carbon monoxide and water, show the absence of such retardation.

Time in minutes,	Pressure increase in mm. H ₂ ,	k	$\frac{1}{t} \log \frac{P_0}{P_\infty}$
110	33	0.000374	
190	56	0.000362	
315	90	0.000389	
395	103	0.000364	
560	140	0.000374	
1215	242	0.000387	
1410	265	0.000397	
1695	295	0.000422	
2000	317	0.000436	
	366		

On the other hand, some accelerating influence of excess of water on the velocity of the carbon dioxide reaction has been observed. Possibly the adsorbed water has a sort of secondary catalytic influence on the neighbouring adsorbed molecules of formic acid, and any drift in the proportions of carbon dioxide in Table II might be attributable to this. The following results illustrate the influence of considerable excesses of water. Formic acid (90 per cent.) was heated in similar bulbs at 209°, in some cases alone and in some cases with about five times its weight of water. Typical analyses of the products were :

	CO.	CO ₂ .
Without excess water	1.24 c.c.	0.02 c.c.
	1.28 c.c.	0.023 c.c.
With excess water	1.044 c.c.	0.057 c.c.
	1.345 c.c.	0.053 c.c.

Again, at 300°, in bulbs made from the same length of glass tubing, 90 per cent. formic acid, heated to nearly complete decomposition, gave 24.5 per cent. and 29.2 per cent. of the carbon dioxide-hydrogen products, whilst when 100 per cent. excess of water was added initially these rose to 50.9 and 46.6 per cent.

The effect of this accelerating influence of water on the values of k_{CO_2} , when there is no excess of water added initially appears to be not very pronounced and is difficult to disentangle from the inevitable variations in the nature of the surface, but attention has already been directed to a possible similar effect in the case of the catalytic decomposition on silver.

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[Received, April 6th, 1923.]

CLVI.—The Ternary System Ammonium Chloride-Ferric Chloride-Water.

By FREDERICK WILLIAM JEFFREY CLENDINNEN.

A CONSIDERABLE amount of work has been carried out on this system by previous workers. Retgers (*Z. physikal. Chem.*, 1892, **9**, 314, 385; 1892, **10**, 550; 1893, **12**, 583) repeated some experiments of Lehmann (*Molekularphysik*, 1883, **1**, 427), and found that ammonium chloride and ferric chloride would mix in the solid state. He also remarked on the form of the crystals obtained. A fuller discussion of the system $NH_4Cl-FeCl_3-H_2O$ at 15° was given by Roozeboom (*Z. physikal. Chem.*, 1892, **10**, 145), who stated that the following solid phases could exist in equilibrium

with various solutions at this temperature: ferric chloride hydrate ($2\text{FeCl}_3 \cdot 12\text{H}_2\text{O}$); the double salt $2\text{NH}_4\text{Cl} \cdot \text{FeCl}_3 \cdot \text{H}_2\text{O}$ (2.1.1) and mixed crystals of ammonium chloride with a ferric chloride content rising to 7 per cent. These mixed crystals showed, however, peculiar irregularities. The ferric chloride content in the crystal showed a considerable increase in general with that of the solution, yet a decrease was shown with some crystals.

The best work recorded is that of Mohr (*Z. physikal. Chem.*, 1898, **27**, 193), who examined the system at 25°, 35°, and 45°. At the lower temperatures, he obtained results similar to those of Roozeboom at 15°, and he also observed the same peculiar irregularities in the compositions of the mixed crystals. At the higher temperatures, he claims to have found two new compounds: $\text{NH}_4\text{Cl} \cdot \text{FeCl}_3$ (1.1.0) and $\text{NH}_4\text{Cl} \cdot 2\text{FeCl}_3 \cdot 4\text{H}_2\text{O}$ (1.2.4), but his method of working was not entirely satisfactory, and it has seemed advisable to study the system more fully. Observations have therefore been carried out which define the equilibria obtaining at 25° and 60°.

The experimental procedure at the lower temperature was similar to that described in a previous paper (Clendinnen and Rivett, T., 1921, **119**, 1329). At the higher temperature, it was found that solutions containing much ferric chloride destroyed the filter-paper used to retain the wet solid, which was therefore caught in a Gooch crucible containing a fine silver gauze plate. The solutions and residues were analysed by standard methods, ammonium by distillation, chloride and iron (when necessary) gravimetrically.

The results obtained at 25° (Table I) are shown, plotted in the usual triangular diagram, in Fig. 1.

TABLE I.
System at 25°.

Density.	Percentage composition.				Solid phases present.
	Solution.		Residue.		
	NH_4Cl .	FeCl_3 .	NH_4Cl .	FeCl_3 .	
1.132	24.14	7.64	87.22	2.57	Mixed crystal series AB.
1.177	21.19	13.26	87.58	3.48	
1.228	18.54	19.27	84.71	5.91	
1.327	16.05	28.97	84.36	7.36	
1.358	16.63	30.45	51.31	46.27	B and C.
1.356	15.59	31.61	33.65	51.93	
1.369	13.41	33.46	34.00	52.98	
1.412	8.70	38.10	29.65	51.41	Mixed crystal series CD.
1.455	5.13	42.82	28.90	52.81	
1.513	2.93	47.63	32.11	55.25	
1.536	2.29	49.50	3.27	55.87	D and 0.1.6.
1.525	1.30	48.80	0.73	53.60	

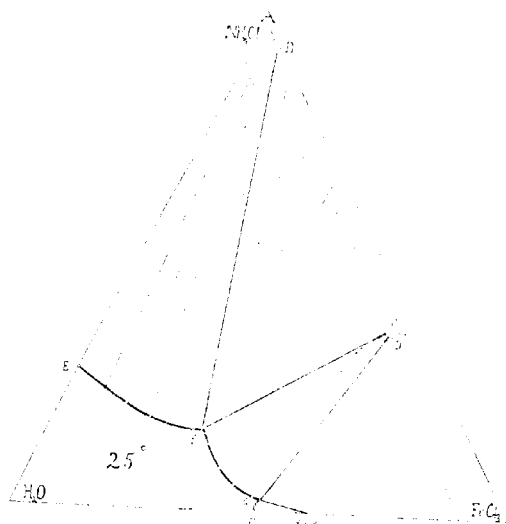
TABLE II.
System at 60°.

Density.	Percentage composition.				Solid phases present.
	Solution.		Residue.		
	NH ₄ Cl.	FeCl ₃ .	NH ₄ Cl.	FeCl ₃ .	
1.133	31.37	7.75	79.14	3.21	Mixed crystal series AB.
1.197	28.02	15.49	80.72	4.98	
1.268	25.40	22.95	72.34	9.45	
1.298	24.73	25.78	38.53	42.82	
1.310	22.49	27.47	35.13	51.36	
—	19.04	30.73	34.32	51.60	B and C.
1.365	16.05	33.25	33.99	52.01	
1.384	13.66	35.84	30.07	50.06	
1.418	10.57	39.20	32.43	53.41	
1.455	7.12	43.96	29.29	53.03	
1.499	5.74	47.41	30.67	54.45	Mixed crystal series CD.
1.534	4.56	53.10	27.07	55.41	
1.565	4.75	55.73	27.46	56.13	
—	5.64	60.31	24.47	58.02	
1.626	7.20	63.60	—	—	
1.639	8.85	65.08	23.18	60.55	D and E, 1, 1, 0
1.643	9.51	65.20	16.61	63.56	
—	9.48	65.40	24.21	62.73	
1.620	8.57	65.70	14.49	69.10	
1.635	7.42	66.35	16.95	71.30	
1.653	5.71	67.44	14.08	70.80	1, 1, 1, 0.
1.677	3.78	69.47	13.22	72.22	
1.695	2.48	71.90	12.65	73.64	
—	2.22	72.74	—	—	
1.722	1.99	73.44	—	—	
1.741	1.81	74.08	12.32	74.52	1, 1, 1, 0.
1.745	1.57	75.37	9.99	75.14	
—	1.15	76.31	3.55	77.54	
1.793	0.40	77.36	3.38	78.70	
—	0.38	77.30	2.48	78.14	
—	0.25	78.10	—	—	1, 1, 1, 0.
—	0.18	78.20	1.12	79.20	
1.798	—	78.42	—	—	1, 1, 1, 0 and 0, 1, 1, 2.

It will be observed that the irregularities found by Roozboom and Mohr (*loc. cit.*) for the compositions of the mixed crystals are not shown here. To ascertain the cause of these irregularities, experiments were carried out in order to observe the effect of time of shaking on the composition of the crystals. Three mixtures of similar composition were made up; one was rotated in a sealed tube in a thermostat for one hour, another for one day, and the third for four days. It was found that the ferric chloride content of the first crystals to separate was relatively high, whereas after one day's shaking the ferric chloride content had fallen to a small value, which remained practically unchanged after four days' shaking. Interesting changes take place in the crystals during this time (compare Retgers, *loc. cit.*; Mohr, *loc. cit.*; van der Kolk, *Z. physikal. Chem.*, 1893, **11**, 167), but further investi-

gation by a crystallographer is necessary. The composition of the crystals depends also on the amount which separates from the mother-liquor. This variation in composition is considered in detail in another paper on the analogous system containing manganous chloride. It is evident, therefore, that a regular series of mixed crystals can be obtained only if one shakes the mixtures for a long time and obtains about the same low ratio of solid to liquid in each case. Failure to maintain constant conditions may account for the irregularities in earlier work.

FIG. 1.



Now consider the question of the compositions of the mixed crystals at the ammonium chloride end (*AB*, Fig. 1). The residue method will not indicate these, and therefore analyses of the dried crystals must be made. An examination of Fig. 1 shows that the maximum amounts of water and ferric chloride in this series of crystals are very small compared with the amount of ammonium chloride, hence any mother-liquor adhering to the dry crystals will introduce a very large error in the ratio of the mols. H_2O per mol. FeCl_3 contained in the crystals. Roozeboom attempted to dry a sample of these crystals, and obtained results which led him to believe that the ratio of mols. H_2O per mol. FeCl_3 was 1 to 1. Retgers, on the other hand, believed the ratio to be 1 to 1.

Several attempts were made to dry these crystals on porous tiles placed in a desiccator over some of the mother-liquor. It was found on analysis that the mols. H_2O per mol. FeCl_3 varied from 3.0 to 5.6 in different samples. The view is taken that these crystals were not quite dry. The quantity of mother-liquor adhering to them need not exceed 1 per cent. in order to reduce the ratio to 1. When crystals belonging to the series CD (Fig. 1), in which there is little doubt that the ratio of mols. H_2O to mols. FeCl_3 is very near unity, were dried in a similar manner, they were found to be still slightly wet. If one assumes that the amount of adhering liquor is the same in each case, then after making allowances for this in the ammonium chloride series, one obtains results which may be represented by points on the line AD . This is in agreement with the view of Rutgers.

Consider now the solids in equilibrium with solutions on the second curve (FG). Both Roozeboom and Mohr state that a single solid is in equilibrium with all solutions on this curve, namely, the double salt 2.1.1. It will be seen from Fig. 1 that the results at 25° do not support this view. The tie-lines converge only approximately to 2.1.1. On close examination it will be seen that actually a mixed-crystal series exists, although with narrow limits. The results at 60° (CD , Fig. 2) show that a similar series exists at that temperature. Every solution represented by a point on the solubility curve, then, is in equilibrium with a different solid (compare Rivett, *Chem. News*, 1921, 123, 251).

When the amount of ammonium chloride in the saturated solution falls below 2.29 per cent., ferric chloride hexahydrate is the solid in equilibrium. No doubt there is a mixed-crystal series here also, but it is quite beyond our power to detect it.

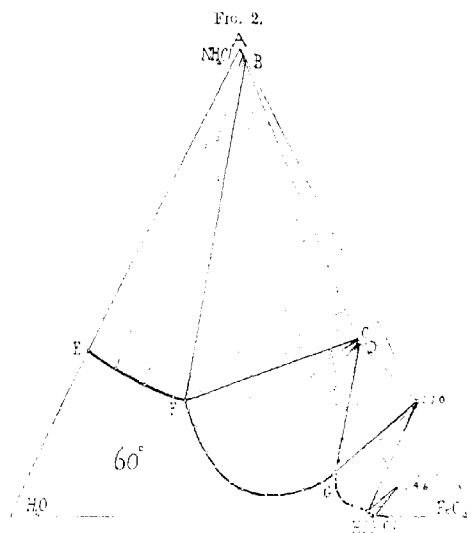
In Fig. 2 the results obtained at 60° are represented. In addition to the two mixed-crystal series mentioned above, three other solid series appear which can be represented by 1.1.0, 1.4.6, and 0.1.2, within the limits of experimental error. The error is greater in those systems containing a large amount of ferric chloride, owing to the densities of the solutions and the fine state of division of some of the crystals making satisfactory separations difficult.

Mohr (*loc. cit.*) mentions the compound 1.1.0, the existence of which is confirmed by this work. But, taking his figures at 45°, the point corresponding with the second new compound he mentions (1.2.4) lies within his heterogeneous region 1.1.0 saturated solution. It cannot therefore be in stable equilibrium with any solution at this temperature.

With regard to the solids in equilibrium with the next curve (HJ), if one looks for simple proportions of the components the

residue method gives a choice of at least two, 1.3.3 and 1.4.6, for it will be observed that the tie-lines pass through both these points within experimental error. Analysis of crystals dried on porous tiles decides in favour of the latter, the ratio of mols. NH_4Cl : mols. FeCl_3 : mols. H_2O being 1 : 4.09 : 6.2.

It is taken as proved, from the work of Roozeboom, that the solid in equilibrium with the solutions along the curve JK is $\text{FeCl}_3 \cdot 2\text{H}_2\text{O}$. Presumably both here and in the 1.1.0 and 1.4.6



cases there exist mixed crystals with differences in composition less than the errors of measurement.

Summary.

1. The work of Roozeboom and Mohr on the compositions of ferric and ammonium chloride mixed crystals has been extended at 25° and 60°.

2. The existence of the alleged compound, $2\text{NH}_4\text{Cl} \cdot \text{FeCl}_3 \cdot \text{H}_2\text{O}$, has not been confirmed. A mixed-crystal series with narrow limits, the members of which approximate to this composition, has been found.

3. The existence of the compound $\text{NH}_4\text{Cl} \cdot \text{FeCl}_3$ mentioned by Mohr has been confirmed at 60°.

4. The compound $\text{NH}_4\text{Cl} \cdot 2\text{FeCl}_3 \cdot 4\text{H}_2\text{O}$, mentioned by Mohr, is theoretically impossible as a stable solid if one takes his figures at 45° . No such compound has been found at 60° .

5. A new solid, $\text{NH}_4\text{Cl} \cdot 4\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, has been found to separate from certain solutions at 60° .

In conclusion, I desire to express my thanks to Dr. A. C. D. Rivett, whose help was invaluable throughout this work.

UNIVERSITY OF MELBOURNE.

Received, April 9th, 1923.

CLVII.—*A Critical Solution Temperature for Solids in the Binary System Ammonium Chloride-Manganous Chloride Dihydrate.*

By FREDERICK WILLIAM JEFFREY CLENDINNEN and ALBERT
CHERBURY DAVID RIVETT.

THE analogy between two-phase systems of liquid-vapour and liquid-liquid appears to have been pointed out first by Nernst (*Z. physikal. Chem.*, 1889, **4**, 383). Later, Masson (*ibid.*, 1891, **7**, 500) developed the comparison in some detail, particularly from the side of temperature influence, and proposed the term "critical solution temperature" for the point of complete miscibility of two liquids experimentally established in several cases by Alexejew (*Wied. Ann.*, 1886, **28**, 305), thus emphasising the likeness between it and the critical temperature of liquid and vapour. Ramsay (*Z. physikal. Chem.*, 1891, **7**, 511) suggested that the similarity would be more correctly shown if one plotted isotherms giving osmotic pressures against specific volumes, instead of the isobars of Masson. The parallelism cannot, however, be regarded as complete, since the lower critical solution temperatures in liquid-liquid systems have no counterpart in liquid-vapour systems (compare Büchner in Roozeboom's "Das Heterogene Gleichgewicht," II, ii, p. 2 onwards).

The recognition of solid solutions by van't Hoff (*Z. physikal. Chem.*, 1890, **5**, 322) might have suggested the possibility of a similar critical solution temperature for a solid-solid binary system, but no case appears to have been described. We have been led by two pieces of evidence to seek for such a point in the system ammonium chloride-manganous chloride dihydrate, investigated through the ternary system containing the two salts and water. In the first place, a glance at the diagrams in an earlier communication (Cleadinnen and Rivett, *T.*, 1921, **119**, 1329) giving

this system at 25° and 60° will show that the break near the ammonium chloride end in the formation of mixed crystals between ammonium chloride and manganous chloride dihydrate is decidedly greater at 60° (*loc. cit.*, p. 1331, line *FG* in Fig. 1) than it is at 25° (p. 1333, Fig. 2). Again, in the very similar system with cobaltous chloride in place of manganous chloride (Clendinnen, T., 1922, **121**, 804), complete miscibility of ammonium chloride and the dihydrate is realised in the corresponding portion of the system at 60°. So that a critical solution temperature in each system would appear to be a possibility. We have confined attention to the former.

To establish the case thoroughly it has been considered necessary to work at 70°, 60°, 50°, 40°, 32.5°, 25°, 20°, and 10°, the experimental procedure being much the same as in the previous paper. As usual, the effect of pressure has been left out of consideration,

TABLE I.
Effect of variation of complex at 25°.

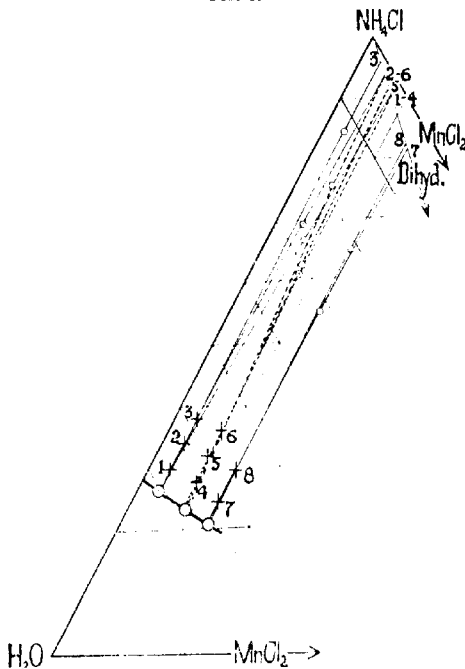
No.	D_4^{25}	Percentage composition.			
		Solution.		Residue.	
		NH ₄ Cl.	MnCl ₂ .	NH ₄ Cl.	MnCl ₂ .
1	1.101	26.56	3.22	66.9	5.59
2	1.101	26.56	3.29	66.2	4.14
3	1.103	26.36	3.56	84.5	3.13
4	1.142	23.65	8.51	61.3	7.58
5	1.144	23.49	8.70	62.9	7.22
6	1.149	23.13	9.32	75.5	5.73
7	1.181	21.14	13.31	55.2	13.87
8	1.186	20.90	13.61	65.2	13.57

since the alteration in solubility brought about by moderate change in pressure is quite negligible. As will be seen, the isotherms obtained leave no room for doubt about the existence of a lower critical solution temperature at a little under 25°; but to determine the precise value of the temperature is another matter. For since the composition of solid phase varies progressively with that of the liquid, it follows that if such an amount of solid as is required for accurate analysis be separated from a solution, its composition is likely to be an average of innumerable layers, each differing slightly from the next, rather than to be throughout that which is in equilibrium with the final liquid. That this is so is clearly seen from Table I and Fig. 1, the latter reproducing a part of a triangular diagram.

Complexes of 50 grams, of mean composition represented by the crosses 1, 2, 3 . . . , were heated to homogeneity in sealed glass tubes and then rapidly cooled to 25° and rotated at that tem-

perature for about twenty-four hours in a thermostat. The analyses of solutions and residues show that when the percentage of manganous chloride is low (as in cases 1, 2, and 3) the composition of the residue varies greatly with that of the complex. The variation, however, is less when the proportion of manganous chloride increases (as in 4, 5, and 6) and has become very small in the region of the complexes 7 and 8. Fortunately, the latter happens to be the

FIG. 1.

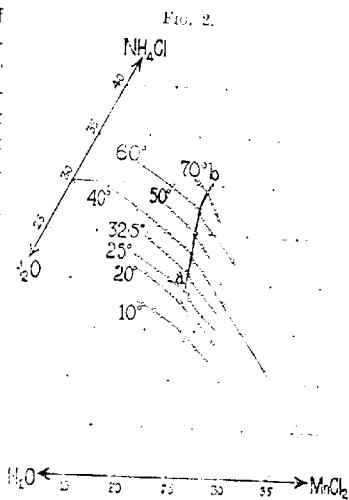


part in which the main portion of this investigation lies. By keeping complexes always of such composition that only about three grams in fifty separate as solid, the doubt as to the precise solid in equilibrium becomes slight, although it remains sufficient to make the determination of the exact critical point uncertain. The difficulty can be overcome, but since we have been concerned with establishing the existence of a critical temperature rather than with its precise determination in a particular instance, the extra work has not seemed worth while.

EXPERIMENTAL.

Table II gives the experimental figures for eight isotherms, the figures quoted for 60° and 25° being additional to those already published, and at 25° correcting some of the latter. Densities (D_4) have been determined for all solutions, and compositions of these and of the residues (wet solids) are given as percentages by weight of ammonium chloride and anhydrous manganous chloride. Water, found by difference, is not quoted. In the last column is the percentage of ammonium chloride in the dry solid, a figure obtained graphically in

each case for the point of intersection in a triangular diagram of the line solution-residue produced and that joining the points corresponding with pure NH_4Cl and $\text{MnCl}_2 \cdot 2\text{H}_2\text{O}$. Fig. 2 shows these results, including some from the previous paper, plotted in a triangle of which only so much is reproduced as is necessary. From 70° to 25° there are two curves intersecting sharply along the line ab . This line is practically straight up to 60° and then is markedly deflected. This change of



direction at higher temperatures will be investigated further if it proves to be of any interest. Below 25°, the points lie on continuous curves. To show this more definitely, one must plot the results rather differently, and probably the simplest way is that reproduced in Fig. 3. As ordinates are taken the percentages of ammonium chloride in liquids (column 3, Table II), and as abscissae the percentages in the dry solids in equilibrium with these (last column, Table II). These curves then fore show the relative distribution of ammonium chloride between liquid and solid phases.

Discussion of Results.

These distribution isotherms permit one to divide the whole field into several regions. *A* and *B* are regions of existence of homogeneous, single-phase, mixed crystals. *C* is a heterogeneous

TABLE II.

Percentage composition.

Temp.	D_L^*	Solution.		Residue.		Dry solid.
		NH ₄ Cl.	MnCl ₂ .	NH ₄ Cl.	MnCl ₂ .	
70°	1-180	30-55	12-13	65-9	17-49	75-6
	1-189	30-11	12-67	50-6	17-46	71-1
	1-195	29-63	13-48	66-7	29-89	69-5
	1-196	29-58	13-43	57-6	21-21	68-4
	1-200	29-38	13-75	49-5	22-23	63-5
	- -	29-28	13-62	54-8	23-32	64-8
	1-201	28-85	13-98	46-2	24-00	59-4
	1-200	28-75	14-28	48-9	27-20	57-3
	1-207	28-10	14-86	46-9	28-15	55-2
	1-207	27-86	14-96	46-3	29-89	53-7
	1-211	27-43	15-60	43-1	31-24	50-2
	1-213	27-11	15-85	40-95	29-59	49-8
	1-219	26-67	16-06	42-4	33-12	48-3
60°	1-187	28-51	12-26	52-1	16-12	73-4
	1-195	27-88	13-34	60-2	20-20	70-8
	1-197	27-69	13-63	59-2	21-02	69-6
	- -	27-53	13-78	56-4	20-49	69-3
	1-197	27-52	13-80	52-6	19-86	69-0
	1-199	27-52	13-90	54-6	20-34	69-1
	1-202	27-40	14-07	51-3	19-93	68-6
	1-204	27-40	14-07	54-85	22-51	66-1
	1-205	27-41	14-05	51-1	22-09	65-3
	1-201	27-35	14-13	55-3	21-77	67-8
	1-202	27-30	14-17	53-1	21-66	67-6
	1-202	27-30	14-18	49-0	21-10	67-4
	1-202	27-25	14-27	60-95	24-56	66-4
	1-205	27-20	14-30	47-6	20-81	65-7
	1-204	27-11	14-52	52-75	22-63	65-3
	- -	27-50	13-85	48-85	24-40	60-8
	1-202	27-15	14-13	41-15	22-87	60-2
	1-200	26-79	14-40	48-1	26-19	59-2
	1-207	26-30	14-94	50-8	31-19	55-5
	1-212	26-27	15-00	45-2	27-22	55-9
	1-213	25-32	16-12	42-2	28-26	53-2
50°	1-168	27-41	11-09	61-5	14-67	78-8
	1-177	26-19	12-04	63-8	17-32	75-3
	1-190	25-85	13-61	59-8	19-01	72-5
	1-200	25-22	14-65	56-82	21-55	68-3
	1-200	24-81	14-89	45-5	24-41	59-6
	1-211	23-79	16-07	49-35	30-66	55-6
	1-2165	23-10	16-94	46-7	31-89	53-2
40°	1-198	29-36	3-98	67-6	5-76	96-5
	1-138	27-34	7-68	61-6	8-02	89-0
	1-150	26-58	9-13	60-3	10-38	85-4
	1-162	25-77	10-62	61-7	11-21	81-2
	1-171	25-07	11-87	66-4	14-05	79-7
	1-181	24-62	12-63	61-3	15-74	77-8
	1-190	24-02	13-68	51-9	16-26	75-6
	1-198	23-48	14-63	52-1	18-01	72-6
	1-206	23-97	15-49	53-7	20-55	69-1
	1-210	22-16	16-09	44-9	24-83	60-2
	1-217	21-55	16-92	46-9	27-78	57-6
	1-226	20-96	17-60	44-8	28-86	55-7
	1-229	20-50	18-30	44-1	30-25	54-0

Two sol-
phases.

Metastable.

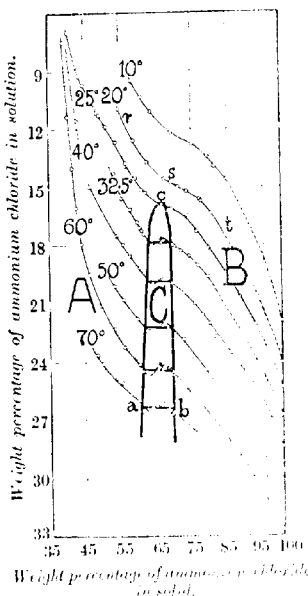
TABLE II.—(continued.)

Temp.	λ'_1	Percentage composition.					
		Solution.		Residue.		Dry solid.	
		NH ₄ Cl.	MnCl ₂ .	NH ₄ Cl.	MnCl ₂ .	NH ₄ Cl.	MnCl ₂ .
40°	1.235	17.98	24.28	29.9	29.8	46.4	
	1.288	14.52	25.16	30.9	36.2	42.7	
	1.326	11.17	29.21	28.0	38.7	40.6	
32.5°	1.168	24.22	10.79	62.4	12.02	83.4	
	1.176	23.25	12.21	53.5	13.10	81.4	
	1.186	22.63	13.35	59.0	15.00	79.3	
	1.195	22.07	14.40	57.1	16.60	76.5	
	1.203	21.56	15.28	59.0	18.43	74.1	
	1.206	21.27	15.64	47.7	18.70	71.7	
	1.211	21.07	16.07	54.8	20.68	70.1	
	1.210	20.98	16.00	54.8	21.01	69.6	
	1.212	20.79	16.39	52.0	21.65	68.0	
	1.216	20.68	16.60	52.2	22.85	66.5	
	1.212	20.84	16.41	49.6	22.41	66.1	
	1.211	20.48	16.20	46.6	24.47	61.5	
	1.213	20.26	16.39	47.65	25.33	60.8	
	1.215	20.41	16.91	45.6	25.33	60.3	
	1.216	20.07	16.86	46.1	25.66	60.1	
	1.218	19.81	17.36	49.4	27.29	59.6	
	1.227	19.18	18.20	45.2	27.73	57.8	
	1.234	18.57	18.97	46.8	30.89	55.1	
	1.249	17.29	20.61	45.7	32.20	53.4	
25°	1.216	19.13	17.00	45.9	26.31	69.25	
	1.218	19.08	17.05	32.5	18.58	69.25	
	1.220	18.89	17.59	46.7	22.08	66.5	
	1.220	18.31	17.50	12.5	23.96	62.0	
	1.222	18.17	17.73	39.9	23.81	60.9	
	1.227	17.48	18.53	46.5	27.22	59.4	
	1.235	16.74	19.63	46.0	29.95	56.5	
	1.251	15.67	21.11	53.8	31.79	53.8	
20°	1.176	20.55	12.27	61.5	12.15	84.2	
	1.195	19.38	14.54	66.4	14.80	80.4	
	1.206	18.69	15.84	58.8	16.75	77.5	
	1.207	18.62	15.93	51.85	16.87	77.2	
	1.213	18.23	16.66	55.8	19.20	73.5	
	1.218	18.09	17.00	54.1	20.67	71.1	
	1.221	17.75	17.44	57.55	22.15	69.2	
	1.222	17.59	17.70	49.0	22.30	67.4	
	1.226	16.74	18.35	46.4	25.19	62.5	
	1.243	15.60	20.18	56.9	29.88	58.8	
	1.263	13.95	22.45	47.5	32.65	54.7	
16°	1.179	17.58	13.53	61.6	12.32	84.8	
	1.193	17.01	14.87	55.8	14.87	81.1	
	1.202	16.46	15.93	54.4	15.69	79.4	
	1.213	15.79	17.40	61.2	18.93	75.1	
	1.223	15.20	18.52	55.6	22.45	69.2	
	1.230	14.41	19.41	53.5	26.73	63.5	
	1.242	13.35	20.77	52.0	28.69	60.9	
	1.250	12.49	22.22	42.4	28.73	58.3	

region, and solids of mean composition represented by points falling within it separate at stable equilibrium into two phases

capable of existing together and with a solution. At 70°, there is a considerable gap, *ab*, between the compositions of co-existing solids. With fall of temperature the gap narrows, or mutual solubility of ammonium chloride and manganous chloride dihydrate increases, showing that the formation of the solid solutions is exothermic. The solids steadily approach one another, the curve *acb* connecting the successive values of the two series of solid phases. At a temperature probably a little below 25°, the regions

Fig. 3.



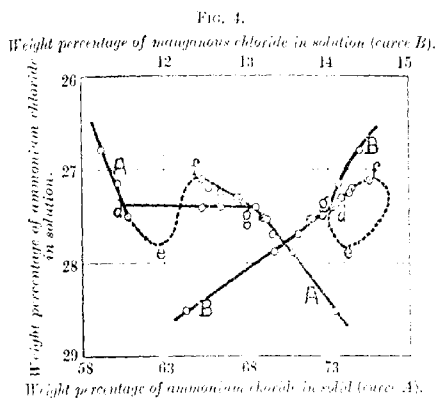
A and *B* merge into one another and the two curves *ac* and *bc* join together. *c* is clearly a (lower) critical solution point, and below it complete miscibility is characteristic of ammonium chloride and the dihydrate within the portion of the binary system studied. Thus at 20° there is no break in the distribution curve *rst*, although there is a most distinct point of inflexion at *r*. At 10°, the inflexion is less, although still very obvious. Measurements have been made also at 0° and -10°, but here irregularities have appeared which suggest formation of metastable solids changing only slowly to stable forms, and further work is necessary; this, however, does not affect the establishment of the critical solid-solution temperature.

At 60° and 32.5°, metastable curves have been followed well into the region *C*. The results at *ac* are plotted on a more open scale in Fig. 4. The radius of the circle round each point is equivalent to one part in eight hundred of the ammonium chloride in solution. Curve *AA'* corresponds with that in Fig. 3, with percentages of ammonium chloride in solution plotted as ordinates against percentages in solid abscissa; curve *BB'* is a solubility curve having the same ordinates, but with percentages of manganous chloride in solution as abscissa.

There can be no doubt that there is continuity along a curve *defg* between the two stable parts. Of this, the part *ef* will be

wholly unstable and unrealisable, whilst *de* and *fg* will be metastable. The latter, *fg*, has been followed very fully, but to obtain points on *de* appears impossible. Except for one point which has not been confirmed, in all cases, even when complexes were allowed as little as half an hour in the thermostat, analyses showed the solids to be either mixtures of *d* and *g* or else to be of compositions representing stages intermediate between metastable (first-formed) solids along *de* and the two stable solids *d* and *g*. At 32.5°, the relations are similar.

For proper comparison with the familiar critical curve (such as that of Andrews for carbon dioxide) obtained by plotting vapour



pressure against specific volumes in the co-existing phases of vapour and liquid, it would be necessary to plot the diffusion pressure of one of the components against its specific volumes in the respective co-existing solids. The diffusion pressures, equal in the two solids, could of course be functions of the osmotic pressure of the same component in the solution with which both solids are in equilibrium. Although it is not possible to obtain these quantities, it is evident from Fig. 3, where weight percentage of ammonium chloride in solution is plotted against that in the solid, that the relationships on the one hand between osmotic pressure and weight percentage of ammonium chloride in the solution, and on the other between its specific volumes and weight percentages in the two solids, are such that the existence of a critical solution temperature remains apparent when these more readily attainable quantities are plotted.

CLVIII.—*The Structure of the Normal Mono-saccharides. Part I. Xylose.*

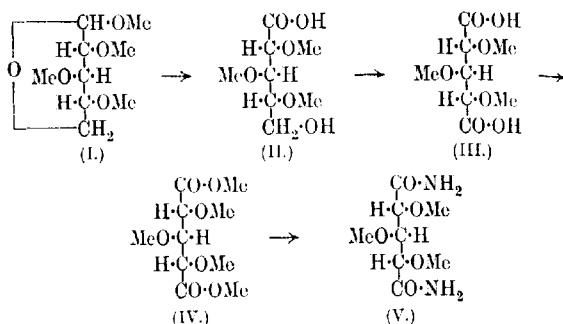
By EDMUND LANGLEY HIRST and CLIFFORD BURROUGH PURVES.

THE prevalent use of the phrase "butylene-oxide sugar" to specify a derivative of the normal or stable type is an indication of the wide extent to which this view of sugar structure has found acceptance amongst organic chemists. The evidence in favour of this particular structure is drawn mainly from a consideration of the spatial relationships of the four valency bonds of the carbon atom, the formation of a five-membered butylene-oxide ring involving little strain in the molecule. Whilst it may be true that the chemical properties of the normal sugars have almost all found a ready interpretation on the assumption of a γ -oxidic linking, nevertheless a review of the recent investigations carried out by Helferich and Malkomes (*Ber.*, 1922, 55, [B¹, 702] and by Bergmann and Mückeley (*ibid.*, 1390) shows that the existence of δ -lactonic rings in sugar derivatives is a possibility that must seriously be taken into consideration. These investigators have found that δ -hydroxy-aldehydes and -ketones react in the form of lactones containing an amylene-oxide ring, and these lactones were found to show a remarkable parallel in their behaviour to aldoses and ketoses. In view of these results, the question of the structure of the oxygen bridge in normal sugars and their derivatives must be regarded as still an open one. The properties of the few ethylene-oxide and propylene-oxide compounds which have been prepared render it very unlikely that either of these structures will be found to be present in normal sugars, but any attempt to make a clear decision between the butylene-oxide and amylene-oxide ring systems is rendered more complicated by the fact that, whilst the δ -hydroxy-aldehyde of Helferich and Malkomes resembles a normal sugar in its behaviour, the δ -hydroxy-ketone prepared by Bergmann and Mückeley is comparable to the γ -sugars.

It is highly desirable in a problem of such fundamental importance as the nature of the oxygen bridge linking in carbohydrates that the conclusions should be based on direct and well-established chemical evidence, and the present series of investigations has been undertaken with the object of securing such evidence. In this communication, results are described which have been obtained from a study of the pentose sugar, xylose. The experimental method adopted follows lines which have been developed by Principal Irvine and his collaborators, and which in their hands

have been applied with uniform success to a whole series of problems in the carbohydrate group. In the first place, the free hydroxyl groups of the sugar molecule are replaced by more stable groupings, so that the possibility of any change in the oxygen bridge linking during the course of the subsequent experiments is either eliminated entirely or rendered easily observable. For this purpose, eminently suitable derivatives are to be found in the fully methylated hexoses and pentoses. The lactone ring in such a compound is then opened up by oxidation and thereafter, by continuing under more drastic conditions, the alcoholic group thus produced is oxidised to carboxyl. A dibasic acid is formed in this way and the nature of the lactone ring in the original sugar is ascertained by identification of the final products of the reaction. Investigations were first carried out with xylose, and the choice of a typical pentose was determined by several considerations. In the first place, the chemistry of the pentoses is considerably less developed than that of the hexoses, and therefore the need for evidence as to structure is all the greater. In addition, oxidation of a methylated pentose presents a simpler case than that of the corresponding hexose derivative, in that a hexylene ring is automatically ruled out of account and an anylene-oxide structure would involve oxidation of a primary alcohol group, which is known to be more readily accomplished than oxidation of the secondary group which would be formed from a hexose derivative possessing the same ring structure. This choice has proved to be singularly fortunate in actual practice, in that xylose has proved to be one of the simpler cases, and the experimental evidence appears to leave little room for doubt that xylose possesses an anylene-oxide structure. Oxidation of β -trimethyl methylxyloside (I) and of trimethyl xylose itself, under considerably more drastic conditions than those usually employed in the sugar group, resulted in an excellent yield of inactive xylotrimethoxyglutaric acid* (III), which was isolated first of all as its dimethyl ester (IV), this being afterwards converted into the diamide (V), and also into the free acid. Analytical data have been obtained for all these derivatives, and in view of the importance of the results the whole series of operations, which may be represented by the scheme given below, has been repeated on different occasions, and identical results have been obtained in each set of experiments.

* Note on nomenclature: The acid has been named in accordance with the nomenclature adopted in the literature for the dibasic acids of the pentose series. These are all trihydroxyglutaric acids and they may conveniently be differentiated by prefixing the name of the sugar from which they are obtainable.

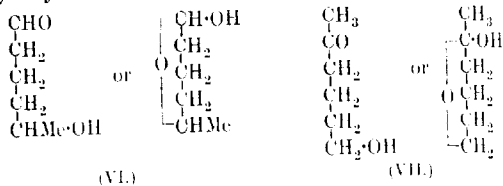


Special interest attaches to the formation of the diamide, which is a crystalline substance and therefore may be obtained in a state of purity definitely free from admixture with other substances. Evidence of this kind is specially welcome in the present case, where the compounds to be identified were syrups, and the homogeneous nature of successive crops of the crystalline amide is by itself practically conclusive evidence that the syrups, which on analysis gave figures corresponding to (III) and (IV), were simple substances, and that xylotrimethoxyglutaric acid had therefore been obtained from methylated xylose. A remarkable peculiarity was displayed during the formation of the amide from the ester by the action of ammonia in methyl-alcoholic solution, the interpretation of which provides a striking confirmation of the presence of glutaric acid derivatives. Before crystals of the amide began to be deposited, the solution turned deep violet in colour, afterwards becoming reddish-brown, whilst the amide itself on being heated in air fused to a dark blue liquid. This may be explained as being due to the formation of the imide of trimethoxyglutaric acid, which then loses methyl alcohol to form a dihydroxydimethoxypyridine. Reference to the work of Rogerson and Thorpe (T., 1905, 57, 1685) shows that dihydroxypyridines are known to oxidise in the presence of oxygen to give blue substances. The change is probably due to the production of a structure similar to that present in indigotin, whilst on further oxidation a deepening of the colour would be expected.

The substances isolated from the oxidation experiments appeared to be perfectly homogeneous, and on several independent occasions identical materials giving the same analytical figures were obtained, but in view of the unexpected nature of the results it was felt that every possible interpretation should be examined. Accordingly, attempts were made to find whether any possible mixture

of compounds might be obtained from xylose which would give results similar to those found by experiment, and from an exhaustive survey of the possible oxidation products obtainable from a fully methylated xylose possessing an ethylene-, propylene-, butylene-, or amylene-oxide structure, it appeared that the only mixture which needed serious consideration as giving approximately the same analytical figures for all derivatives (acid, methyl ester, and amide) as those actually found was one composed of dimethoxysuccinic acid (50 per cent.) and trimethoxyxylonic acid (50 per cent.), which might be derived from xylose if the sugar had a butylene-oxidic linking. It quickly became apparent, however, that the product isolated could not possibly consist of this particular mixture. An examination of the stereochemical configuration of xylose shows that this dimethoxysuccinic acid and its ester should be optically active in the dextrorotatory sense. Xylonic acid shows only slight activity and therefore it is probable that a mixture of trimethoxyxylonic acid with dimethoxysuccinic acid would be optically active. The product actually isolated was definitely inactive. That this inactivity was not due to racemisation during the vigorous oxidation process was proved by the observation that the more reactive *d*-tartaric acid showed no sign of racemisation when treated under the same conditions. Furthermore, the diamide of dimethoxysuccinic acid is readily obtainable from the ester, and is a well-characterised and easily identified substance (Purdie and Irvine, T., 1901, 79, 960). The fact that no trace of this substance was formed during any of the preparations of the amide now described points strongly to the complete absence of dimethoxysuccinic acid, and provides additional evidence in favour of the conclusion that oxidation of methylated xylose gives a dibasic acid without loss of a methoxyl group. A result of this nature would be quite impossible assuming a butylene-oxide structure in the original sugar, and therefore the experimental evidence here described would appear to indicate definitely that xylose possesses an amylene-oxide linking, a result with which the chemical properties are in complete agreement. Most of the reactions of the sugar may be explained equally well on the basis of either a butylene- or an amylene-oxide ring structure, but certain characteristic properties, such as the ready transformation to furfural, can be more easily understood on the basis of the new formula. Thus the production of a furan ring with a free aldehyde group involves the formation of an oxygen bridge linking between the second and the fifth carbon atom of the chain, and this would be expected to take place more readily if the fifth carbon atom was already involved in a linking of this type. It

is especially interesting that xylose should have this type of ring structure, in view of the evidence obtained by Haworth and Linnell (this vol., p. 294) and by Haworth and Mitchell (*ibid.*, p. 301) that an amylenic-oxide ring is present in tetramethyl γ -fructose. Methylated xylose does not show the characteristic reactivity and instability of γ -sugars, but reference once more to the behaviour of the δ -hydroxy-aldehyde (VI) of Helferich and Malkomes as compared with the much greater reactivity of acetylbutyl alcohol (VII), investigated by Bergmann and Mückeley, shows that there is not of necessity any incompatibility in the two results, for xylose corresponds to the hydroxy-aldehyde, which has properties resembling those of the normal sugars, whilst fructose corresponds to the acetylbutyl alcohol, with properties similar to those of γ -sugars.



As the result of experiments conducted with xylose alone, it cannot be claimed that the structure of the normal pentoses or hexoses in general is of the amylenic-oxide type, and the whole trend of the argument advanced is to emphasise the need for independent structural investigation in the case of each of the sugars, and it is proposed to extend on these lines the work which is described in the present paper.

EXPERIMENTAL.

The trimethyl methylxyloside and the trimethyl xylose required as starting materials for the present investigation were prepared from xylose in the manner already described (Carruthers and Hirst, T., 1922, **121**, 2299), the xylose itself being obtained from esparto cellulose (Hirst, *Brit. Assoc. Reports*, 1922; *J. Soc. Chem. Ind.*, 1922, **41**, 3923). The alkylation of the sugar proceeded normally to give 5-trimethyl methylxyloside and thus requires no further comment.

*Oxidation of Trimethyl Methylxyloside.** Complete details are

* An important economy in material was effected as a result of the observation that equally good yields of product, identical with that obtainable from the free sugar, could be isolated by oxidising the corresponding methylxyloside. When the low yield of trimethyl xylose obtainable from trimethyl methylxyloside is recalled (Carruthers and Hirst, *loc. cit.*), the saving both of time and material is found to be considerable. The method is obviously of importance in other similar cases.

given for one oxidation only, but the series of operations has been carried out on other occasions also, both with trimethyl methylxyloside and with trimethyl xylose, to give results identical with those described. In one case, a further account of which is given below, the isolation of the products was rendered more complicated owing to the presence of some incompletely oxidised material, but here also the main product proved to be the same as that obtained in each of the other experiments. Crystalline trimethyl methylxyloside (5.0 grams) was dissolved in 80 c.c. of nitric acid (d 1.20), and the temperature of the solution maintained at 90° until the reaction commenced. The temperature was then lowered to 80° and kept at this point for a period of six hours, until the evolution of oxides of nitrogen, which at first took place very vigorously, had ceased entirely. The clear, colourless solution was then diluted with an equal bulk of water, and the greater part of the nitric acid removed by distillation under diminished pressure from a water-bath at 50° , water being added continuously as distillation proceeded, until altogether some 2 litres had passed through the apparatus. On concentration to a syrup under the same conditions, a colourless glass was obtained which still reacted strongly acid to congo-red. This was dissolved in methyl alcohol, and the solvent distilled away to remove the last traces of water from the system, after which the syrup was treated with 60 c.c. of methyl alcohol containing 3 per cent. of hydrogen chloride. Esterification of the carboxyl groups was effected by boiling the solution for six hours under a reflux condenser. Silver carbonate was used to remove the hydrochloric acid and on evaporating the neutralised solution a syrup was obtained which contained some silver nitrate, formed from the nitric acid which still remained in the system. This was eliminated by dissolving the syrup in ether and filtering, the inorganic material being insoluble. After removing the ether, a neutral, yellow syrup resulted which was purified by fractional distillation under diminished pressure. The isolation of the oxidation products in the form of their methyl esters was found to be much more convenient than attempting a direct examination of the free acids, for adoption of this method of procedure rendered possible the separation and purification of the reaction products by simple distillation. From the original 5.0 grams of trimethyl methylxyloside the following fractions were obtained:

I. 4.2 Grams, b. p. $132-12$ mm. (bath 154°); n_D^{20} 1.4402, the last portion of the fraction showing n_D^{20} 1.4408.

II. 0.3 Gram, b. p. $140-160$, 12 mm.; n_D^{20} 1.4418.

III. Still residue negligible.

Methyl Xylo-trimethoxyglutarate.—The main fraction * was a
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colourless, mobile oil which could not be induced to crystallise. It had the chemical properties of an ester, did not reduce Fehling's solution even on continued boiling, and was soluble in all the usual organic solvents, solution in water being accomplished without hydrolysis of the ester. It was optically inactive in methyl-alcoholic solution under conditions ($c = 2$, $l = 2$) where a specific rotation of $\pm 1^\circ$ would easily have been detectable. The analytical figures and the optical inactivity showed it to be the dimethyl ester of an inactive trimethoxyglutaric acid [Found: C = 48.0; H = 7.5; OMe = 60.5; CO₂Me = 46.6. (CH₃OMe)₃(CO₂Me)₂ requires C = 48.0; H = 7.2; OMe = 62; CO₂Me = 47.2 per cent.]. The carboxyl groups were estimated by hydrolysis of a weighed quantity of the ester with a known excess of caustic soda solution. The molecular weight of the ester in benzene solution was found by the cryoscopic method to be 242 (calc., 250). The yield of analytically pure material amounted to 70 per cent. of the calculated quantity.

Xylo-trimethoxyglutaric Acid.—The ester was warmed with excess of a solution of barium hydroxide in water for one hour at 80–90°, the barium was removed as sulphate by the addition of the exact quantity of sulphuric acid, and the colourless solution was evaporated to dryness under diminished pressure. In this manner a viscous, yellow syrup was obtained which at the ordinary temperature was almost a glass. Treatment at 100° in a vacuum did not result in the formation of any lactone or anhydride, the reaction towards alkali being thereafter that of a typical acid, giving a sharp end-point on titration in the cold with phenolphthalein as indicator. The acid did not reduce Fehling's solution even at the boiling point. It was found to be very soluble in water, somewhat less soluble in methyl or ethyl alcohol and in chloroform. It proved to be impossible to characterise it readily in the form of a salt, since the neutral thallium salt was a glass, the barium salt was amorphous and syrupy, and attempts to obtain crystalline derivatives with alkaloid bases were equally unsuccessful. The acid was optically inactive, observations being made both for the aqueous and the ethyl-alcoholic solutions. Analysis showed it to be trimethoxyglutaric acid [Found: C = 43.2; H = 6.44; OMe = 40.6; CO₂H = 39.9. (CH₃OMe)₃(CO₂H)₂ requires C = 43.2; H = 6.36; OMe = 41.9; CO₂H = 40.5 per cent.].

Diamide of Xylo-trimethoxyglutaric Acid. One gram of the dimethyl ester was dissolved in 6 c.c. of methyl alcohol which had been saturated with ammonia gas at 0°. After four days at room temperature in a stoppered tube, the solution developed a deep blue colour and on the fifth day crystals began to be deposited.

At the end of ten days, formation of the amide was complete and on evaporation to small volume a further quantity of crystals was obtained, the mother-liquors by this time being reddish-brown in colour. After filtration, the solid was washed successively with methyl alcohol and ether and finally dried in the steam-oven. The crystals thus prepared (0.32 gram) were white, melted sharply at $194-195^{\circ}$, and were slightly soluble in the cold in water, ether, or methyl or ethyl alcohol, and dissolved more readily in these solvents at higher temperatures. Recrystallisation could be carried out easily from a mixture of ether and ethyl alcohol, the recrystallised specimen melting at 195° . From solution in methyl alcohol, the amide was obtained in short rods of characteristic appearance under the microscope. Ammonia was evolved when the substance was heated in air, the melt becoming first of all deep blue and afterwards brown. The crystalline appearance, the failure to sublime when heated, the solubilities, and the melting point all sharply distinguish this compound from the diamide of dimethoxy-succinic acid, and its identity as the diamide of xylo-trimethoxyglutaric acid was confirmed on analysis [Found: C = 43.8; H = 7.55; N = 13.0 (by Dumas's method); OMe = 41.7. $(\text{CH}_3\text{OMe})_3(\text{CO}\cdot\text{NH}_2)_2$ requires C = 43.6; H = 7.27; N = 12.73; OMe = 42.3 per cent.]. The esters derived from the different oxidation experiments all gave the same amide, and the same succession of colour changes was observed during the preparation of the amide. Blank experiments definitely proved that the formation of the highly coloured derivatives was dependent on transformations undergone by the ester and was not caused by adventitious impurities present in the methyl alcohol. On account of the ease and certainty of its preparation and the readiness with which the pure compound may be obtained, the diamide forms the most suitable derivative of xylo-trimethoxyglutaric acid as yet available for identification purposes.

Confirmatory Experiments.

Three of the four oxidations carried out gave results practically identical with those just described, but in one case, in which the reaction was stopped before the nitric acid solution had become quite colourless, slight differences were found. 9.2 Grams of trimethylmethylxyloside gave 8.35 grams of ester (b. p. $132-132\frac{1}{2}^{\circ}$ mm.; n_D^{20} 1.4380; $[\alpha]_D^{20}$ $\div 7.7^{\circ}$ in methyl alcohol, $c = 1.74$). The analytical figures did not correspond with those required for any single substance (Found: C = 47.0; H = 7.25; OMe = 34.6 per cent.), and the components of the mixture were separated in the following manner. The syrup (6 grams) was hydrolysed with

baryta, and alcohol gradually added to the resulting aqueous solution of the barium salts. A fractional precipitation of barium derivatives took place, the first portion of which was rejected. The remainder was treated in the usual way to give the free acid (3.5 grams), and this proved to be optically inactive and identical both in physical and chemical properties with the trimethoxyglutaric acid already described (Found: C = 43.1; H = 6.48; OMe = 41.6; CO₂H = 39.6 per cent.). Esterification in the usual manner gave an ester identical with that previously identified as the dimethyl ester of xylo-trimethoxyglutaric acid (b. p. 129°/9 mm., n_D^{20} 1.4368) (Found: C = 48.0; H = 7.38; OMe = 61.5; CO₂Me = 47.8 per cent.). On treatment with ammonia in methyl-alcoholic solution, the diamide (m. p. 195°) was obtained, the formation being accompanied by the characteristic colour changes recorded above (yield 35 per cent. In other preparations, yields varying from 30—40 per cent. were found). There can be no doubt, therefore, that in this oxidation also the main product was trimethoxyglutaric acid.

In view of the lengthy treatment with hot nitric acid to which the oxidation products were subjected, the possibility existed that the optical inactivity of these compounds might be due to racemisation. Test experiments were accordingly carried out under the actual conditions employed during the oxidations to investigate the racemising action of nitric acid. It was found that with *d*-tartaric acid, which may be expected to be more sensitive to racemising influences than the more stable methylated acids, no change in the optical rotatory power was observable after six hours at 90° with nitric acid of density 1.2 (Found: $\alpha_D = 1.13^\circ$; $l = 2$, $c = 15.0$). Inactivation of the oxidation products by racemisation must therefore be regarded as highly improbable.

The authors desire to express their gratitude to the Trustees of the Carnegie Trust for a grant which enabled the work to be carried out.

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CLIX.—*The Chemistry of the Three-carbon System.*
Part I. The Influence of the cyclohexane Ring
on the $\alpha\beta$ - $\beta\gamma$ Change.

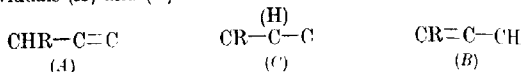
By STANLEY FRANCIS BIRCH, GEORGE ARMAND ROBERT KON,
 and WOODFORD STANLEY GOWAN PLUCKNETT NORRIS
 [With an Introductory Note by Prof. J. F. THORPE].

INTRODUCTORY NOTE.

USING the term tautomerism to mean reversible isomeric change in its widest sense (compare Kon, Stevenson, and Thorpe, T., 1922, 421, 650), it follows that there are two distinct manifestations of the phenomenon which, for the moment, do not appear to bear any relationship to one another. The first, which may be termed the "aromatic" manifestation, because its occurrence is associated with the development of aromatic character, entails valency interchange unaccompanied by the movement of a hydrogen atom. The second, which may be regarded for similar reasons as the "aliphatic" manifestation, involves the movement of a hydrogen atom from one element terminating a tautomeric system to that terminating the system at the other end. The classical example of ethyl acetoacetate, which is the best known illustration of the keto-enol change $\text{CH}_3\text{—C(=O)—CH}_2\text{—CO}_2\text{C}_2\text{H}_5 \rightleftharpoons \text{CH}_3\text{—C(OH)=CH—CO}_2\text{C}_2\text{H}_5$, may be taken as typical of the second manifestation, and benzene the one in which the first is in evidence.

When, however, the chemistry of the three-carbon system, $\text{RCH}_2\text{—C}\equiv\text{C—CH}_3 \rightleftharpoons \text{RC}\equiv\text{C—CH}_2$, is collated, it is evident that there are certain, apparently fundamental, differences between it and that of the keto-enol system, because the chemistry which has hitherto been associated with the three-carbon system is that which, for want of a better name, has been called the chemistry of the glutaconic or semi-aromatic type, in which the occurrence of a normal or semi-aromatic form has been postulated. This form has, up to the present, found no counterpart in other systems exhibiting tautomeric change, and its occurrence seems to show that the kind of tautomerism exhibited by the three-carbon system is of a different order from that shown by any other three-elemental system, and that it ought, therefore, to be placed in a class by itself. But it is unreasonable to suppose that the general principles underlying tautomerism of all three-elemental systems are not based on the same plan, and it is, in the highest degree, desirable to make every effort to bring these principles into line before placing any phenomena arising from them into water-tight compartments. If this is done, the following conclusions are drawn.

(1) In an asymmetrical glutaconic system, as in a symmetrical system, the normal form (C) is intermediate between the tautomeric individuals (A) and (B) :



This follows because the existence of the normal form has been proved thus :

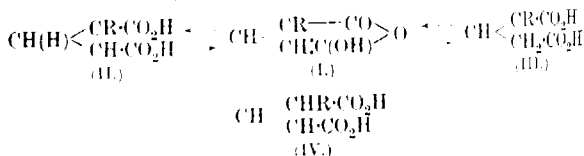
(a) α -Methylglutaconic acid exists in a normal and a labile modification which are both *cis*-forms, and are related to one another, chemically, in precisely the same manner as the two forms of β -methylglutaconic acid.

(b) β -Methylglutaconic acid exists in two forms, called by us the normal and labile forms, which bear exactly the same chemical relationship to one another as do the α -methylglutaconic acids. Nevertheless, in this case, the possibility of isomerism, based on our present system of formulation, is narrowed down to that of the *cis*- and *trans*-type, owing to the position of the methyl group.

This is indeed the view of the structure of these acids advocated by Feist.

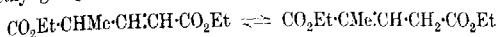
(c) The esters (methyl and ethyl) of methylcyclopropenedicarboxylic acid exist each in three forms, one enol and two keto (Goss, Ingold, and Thorpe, this vol., p. 327). In this case the question of *cis-trans*-isomerism does not arise and therefore one of the keto-esters must have the normal form, which means that the hydrogen atom cannot be placed on any element present in the formula.

The occurrence of the normal form between the two potentially tautomeric individuals (A) and (B) can be proved by a number of experimental facts, but is probably best illustrated by the formation of the hydroxy-anhydride (I) from the normal acid (II) and the hydration of the hydroxy-anhydride under special conditions to the labile acid (III) :



The other tautomeric individual (IV) cannot, in this case, be produced, because its formation would necessitate the passage of the mobile hydrogen atom through its more stable (normal) position in the three-carbon system. It has already been shown that when it does pass out of this position to form, for example, the hydroxy-

anhydride, it passes away from the carbon atom carrying the methyl group. Feist's view that the esters



are tautomeric and that the identity of the α - and γ -positions in glutaconic acid is due to this cause, cannot therefore be correct, and the fact that he obtained two pairs of decomposition products, each pair corresponding with each tautomeric individual, by the aid of ozone merely shows that the normal ester ozonises, as one would expect it to do, as if it were a mixture of the two tautomeric individuals of which it is the intermediate phase, and also that the labile ester passes partly into the normal ester during ozonisation. The marked difference in the behaviour of the normal and the labile ester towards additive reagents of the type of ethyl cyanoacetate is in itself absolute proof that they cannot be related as the tautomeric individuals (A) and (B).

It is evident, however, that conditions may arise, in the glutaconic series and elsewhere, which will so far diminish the stability of the normal form as to render it merely a passing phase in the change between the individuals (A) and (B). Indeed the definite proof which has now been given of the existence of a normal form in all probability supplies the link which has hitherto been lacking connecting the two tautomeric individuals in all three-elemental systems, and therefore we have at hand an explanation of the mechanism by which this change occurs. If this is so it follows:

(2) That definite three-carbon tautomerism will be detected of the type

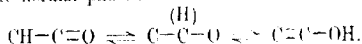


corresponding with the keto-enol change



in which the occurrence of the intermediate normal phase is masked; and

(3) That the keto-enol change itself takes place through an intermediate normal phase:



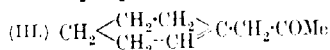
In the ensuing paper we have now definite proof that proposition (2) is true, but as regards proposition (3), we have at present no definite experimental evidence that can be recognised as such. Still it must be accepted, unless we are to adopt the wholly unreasonable view that two exactly similar types of phenomena, in the three-carbon and keto-enol systems, possess totally different mechanisms.

With this paper it has been thought desirable to start a new series, because although the subject now discussed is closely allied to the chemistry of the glutamic acids, it covers a wider field.

It is our purpose in this series of investigations to examine the conditions leading, in the three-carbon or propene series, either to stable normal forms of the glutamic type, or to the production of equilibrium mixtures of tautomeric individuals analogous to the keto- and enol forms of ethyl acetoacetate.

Now it is, we think, evident that the stability of the normal form of the glutamic acids is due to the symmetry of the fundamental glutamic complex, $\text{CO}_2\text{H}\cdot\text{C}\cdot\text{C}(\text{H})\cdot\text{C}\cdot\text{CO}_2\text{H}$, which is so great that this form can be isolated even when the alkyl substitution is asymmetrical. Hence we should not hope to isolate this form of an acid containing a propene system to which only one carboxyl group is attached. If, therefore, under suitable conditions, two isomeric $\beta\gamma$ - and $\alpha\beta$ -unsaturated monobasic acids are of comparable stability, reversible isomerisation, analogous to the keto-enol change, may reasonably be expected.

Actually Fittig has shown (*Annalen*, 1894, **283**, 47) that although the acids (I) and (II) are distinct individuals, each perfectly stable, their sodium salts are interconvertible in aqueous solution.



Since a mixture of acids is obtained on acidification of the equilibrated solution, reversible isomeric change, that is, tautomerism (Kon, Stevenson, and Thorpe, *loc. cit.*), must occur.

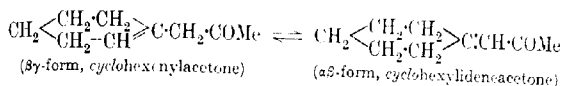
Now on this definition of tautomerism the distinction between rapid and slow interconversion of isomerides is to be regarded as purely artificial. The existence may therefore be anticipated of a compound, structurally similar to Fittig's acids, in which the tautomeric interchange between the $\alpha\beta$ - and the $\beta\gamma$ -forms is so rapid that an equilibrium is produced actually in solution, or in the liquid state. The chemistry of such a compound is described in this communication.

Some time ago, Wallach prepared a ketone, $\text{C}_5\text{H}_{10}\text{O}$, by condensing *cyclohexanone* with acetone (*Annalen*, 1912, **394**, 376; compare also *Ber.*, 1896, **29**, 2955) and assigned to it the constitution (III); similar compounds were produced from the three methyl*cyclohexanones*. Later, one of us obtained the same ketone, *cyclohexenylacetone*, and the corresponding *cyclopentane*- and *cycloheptane*-compounds by a different method (Kon, T., 1921, **119**).

810), and similar constitutional formulæ were adopted for them. The reasons for assigning these formulæ were mainly the normal optical behaviour of the ketones (absence of exaltation), their inability to form additive products with hydroxylamine and semicarbazide, and the difficulty experienced in reducing the double bond by means of hydrogen and palladium.

Norris and Thorpe (T., 1921, **119**, 1199) found, however, that these compounds readily condense with ethyl sodiomalonate, forming derivatives of dihydroresorcinol, a behaviour characteristic of $\alpha\beta$ -unsaturated ketones; they therefore suggested that the formulæ adopted by Wallach and by Kon were incorrect and that the ketones should be represented by the general formula $(CH_2)_n > C:CH \cdot C(OMe)_2$.

The very ambiguity in the chemical behaviour of cyclohexenylacetone and its homologues appeared to be a clue to their true nature; the evidence accumulated up to the present shows, we think, quite conclusively that cyclohexenylacetone (and probably a number of other similar compounds) is a tautomeric substance reacting in the forms

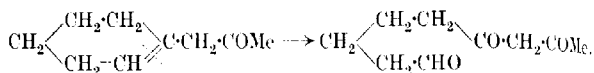


and forming equilibrium mixtures of the two individuals at the ordinary temperature.

In the first place, an attempt was made to settle the problem by synthesis. The excellent method of Blaise and Maire (*Ann. Chim. Phys.*, 1908, [viii], **15**, 556), consisting in the interaction of a zinc alkyl halide and an acid chloride, $R \cdot Zn \cdot Hal + R' \cdot COCl \rightarrow R' \cdot COR$, appeared to be particularly suited to our purpose. The two acids Δ^1 -cyclohexeneacetic acid and cyclohexylideneacetic acid are quite distinct and readily characterised: special experiments were made to make certain that no isomerisation occurred when they were converted into their acid chlorides. It was therefore surprising to find that when the two acid chlorides derived from the carefully purified acids were treated with zinc methyl iodide, the same ketone was produced. It had the same physical properties, gave the same semicarbazone, and condensed with ethyl malonate to form Norris and Thorpe's dihydroresorcinol (*loc. cit.*).

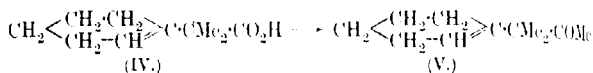
The formation of this derivative is, as Norris and Thorpe rightly point out, very strong evidence of the $\alpha\beta$ -unsaturated structure of the ketone; and, as a yield of more than 80 per cent. of the dihydroresorcinol derivative can be obtained in this reaction, it is clear that the ketone must contain at least a corresponding amount of the $\alpha\beta$ -form. On the other hand, the oxidation of the substance

by means of ozone does not yield any trace of *cyclohexanone*, which would be expected if the substance reacted in the $\alpha\beta$ -form. The products actually obtained have not yet been fully characterised, but it appears probable that the greater part consists of a substance analogous to that obtained by Harding, Haworth, and Perkin (T., 1908, **93**, 1949) on oxidising ethyl Δ^1 -*cyclohexeneacetate*, and formed according to the following scheme :



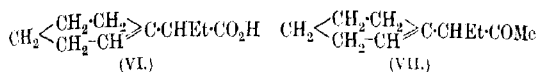
It is a viscous oil which is strongly enolic and acidic in nature.

The evidence of the physical properties, when this is not supported by chemical evidence, has to be accepted with caution, and for this reason it was thought desirable to compare the properties of our substance with those of related substances of known constitution. The ketone (V) was therefore prepared from the acid (IV)



It is clear that this ketone cannot have the alternative $\alpha\beta$ -unsaturated structure; its optical properties are quite normal and comparable with those of *cyclohexenylacetone*. It may be noted in passing that whilst ethyl Δ^1 -*cyclohexeneacetate* has a normal molecular refractivity, the isomeric ethyl *cyclohexylideneacetate* shows considerable exaltation; we have repeated Auwers and Ellinger's observations on this point and can confirm them.

The final proof of the tautomeric nature of *cyclohexenylacetone* was obtained when it was discovered that this ketone contained a mobile hydrogen atom. Its alcoholic solutions give a faint brown coloration with ferric chloride; when mixed with a solution of sodium ethoxide, a deep orange solution is formed, and by the action of ethyl iodide on this solution, the ethyl derivative is readily obtained, the yield exceeding 30 per cent. It is clear that the reaction takes place in the following way: $\text{C} \cdot \text{CH}_2 \cdot \text{COMe} \longrightarrow \text{C} \cdot \text{CH}(\text{ONa})\text{Me} \longrightarrow \text{C} \cdot \text{CHEt} \cdot \text{COMe}$, the ketone reacting in the $\beta\gamma$ -form. It appears very unlikely that the $\alpha\beta$ -form would be able to undergo this reaction, and the enolisation cannot take place at the expense of the terminal methyl group, because the entering alkyl group would then be attached to the terminal carbon atom. This is not the case, as the new ketone has been synthesised from α - Δ^1 -*cyclohexenylbutyric acid* (VI) and zinc methyl iodide and must have the formula (VII).



The ordinary form of the compound, judging by its normal optical properties, is the $\beta\gamma$ -form; nevertheless, the introduction of the alkyl group prevents further alkylation, doubtless owing to the reluctance of the tautomeric system to part with the last mobile hydrogen atom (compare Kon and Thorpe, T., 1922, **121**, 1795). Neither does this ketone condense with ethyl sodiomalonate; this we ascribe to the inhibiting action of the α -ethyl group.

The yield of ethylated ketone derived from the $\beta\gamma$ -form of cyclohexenylacetone is, as already stated, more than 30 per cent.; and as more than 80 per cent. of dihydroorecinol derivative, formed from the $\alpha\beta$ -form, can also be obtained, it is evident that some conversion of one form into the other must occur in the presence of sodium ethoxide and that the substance is, in fact, tautomeric.

It is felt that the experimental evidence at our disposal is, as yet, too incomplete to allow definite conclusions to be drawn as to the causes of tautomerism in the substances dealt with in this paper, and for this reason it is proposed to extend the investigation to a large number of similarly constituted compounds in the near future.

Attention might, however, be directed to two factors which probably determine the mobility of the three-carbon system in cyclohexenylacetone. It is possible to picture a competition between two opposed forces, one favouring the $\alpha\beta$ -, the other the $\beta\gamma$ -form. The first is due to the presence of the carbonyl group, which possesses a strong tendency to become conjugated with a double linking; the great readiness with which $\alpha\beta$ -unsaturated ketones and acids are produced need scarcely be emphasised.

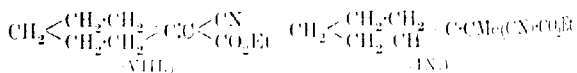
On the other hand, the cyclohexane ring (and also the cyclopentane and cycloheptane rings) possesses a very considerable tendency to acquire one or more double bonds. For example, methylenecyclohexane passes into 1-methyl- Δ^1 -cyclohexene on being warmed with alcoholic sulphuric acid (Wallach, *Annalen*, 1908, **359**, 287); moreover, Dieckmann showed (*Annalen*, 1901, **317**, 27) that ethyl cyclohexanonecarboxylate (or its 5-ring analogue) is much more enolic than ethyl acetoacetate. This doubtless accounts for the transformation (Beesley, Ingold, and Thorpe, T., 1915, **107**, 1080) of cyclohexylideneacetic acid into Δ^1 -cyclohexeneacetic acid through the agency of 64 per cent. aqueous potassium hydroxide, and for the parallel conversion of ethyl cyclohexylideneacetate into ethyl Δ^1 -cyclohexeneacetate which has now been effected by heating the former with moist potassium hydrogen sulphate. The change from the $\alpha\beta$ -unsaturated to the $\beta\gamma$ -unsaturated acid (or ester) appears,

indeed, to be complete, no equilibrium being reached, in direct contrast to the behaviour of Fittig's acids (see above). The presence of the *cyclohexane* ring will thus favour the production of the $\beta\gamma$ -form of the ketone. It seems unlikely at first sight that the latter would be produced to any extent in preference to the conjugated $\alpha\beta$ -form, but consideration will show that the $\beta\gamma$ -form can also be represented as possessing a system of conjugated double linkings, namely, in its enol form: $\text{C}=\text{CH}^*\text{CMe}^*\text{OH}$. The existence of such a form is proved by the fact that the ketone gives a faint coloration with alcoholic ferric chloride and is readily alkylated in the position

In order that a three-carbon system may become mobile, the two opposed forces acting on the double linking must not only be approximately equal on their relative magnitudes depends the position of equilibrium—but they must be sufficiently great; and on this the degree of mobility of a system appears to depend. This consideration may account for the static nature of the ester of Δ^1 -*cyclohexene*- and *cyclohexylidene*-acetic acids, for it is well known that carbethoxyl is a much less powerful "activating group" than carbonyl in causing the mobility of an α -hydrogen atom (compare, for instance, acetylacetone and ethyl acetoacetate; see also *Annual Reports*, 1922, **19**, 103).

The action of reagents on *cyclohexenyl*acetone is readily understood, and in this respect the substance is quite analogous to other tautomeric substances; the reagent unites with one form—no matter how small the amount originally present—and more of that form is immediately produced to restore the equilibrium.

While this investigation was in progress Lapworth and McRae published their observations on certain esters obtained by the condensation of ethyl cyanoacetate with aldehydes and ketones (T., 1922, **121**, 2741). They show that, in general, these substances react like $\alpha\beta$ -unsaturated compounds of the general formula $\text{RR}'\text{C}=\text{CH}^*\text{C}(\text{CN})\text{CO}_2\text{R}$, including ethyl α -cyanocyclohexylidenecetate (VIII), which was originally prepared by Harding, Haworth, and Perkin (*loc. cit.*). These authors assigned to it the $\beta\gamma$ -unsaturated structure, owing to the fact that an alkyl (or phenacyl) group can be readily introduced in the α -position; the substituted ester (IX) must, of course, have the $\beta\gamma$ -structure.



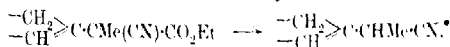
Lapworth and McRae assume that when the sodium-derivative is formed from the parent ester a hydrogen atom is probably

"borrowed" from the γ -position, the sodio-derivative being derived from the $\beta\gamma$ -form; this structure is retained when an alkyl group replaces the sodium atom, and it is shown that the alkylated substance no longer undergoes the condensation reactions characteristic of the parent substance. Ethyl α -cyanoheptylideneacetate, a straight-chain compound, does not yield a phenacyl derivative and alkylates, apparently, with some difficulty. These facts are, we think, capable of ready interpretation in the light of the views put forward in the present communication.

In the first place, it would appear highly probable that ethyl α -cyano- Δ^1 -cyclohexeneacetate is a tautomeric substance in the same way as cyclohexenylacetone, but with the equilibrium greatly on the side of the $\alpha\beta$ -form (this does not differ materially from the view expressed by Lapworth and McRae, *loc. cit.*, p. 2745). That the substance reacts in this form is abundantly proved by Lapworth and McRae's experiments, in addition to which we have been able to condense the ester with ethyl cyanoacetate and ammonia by Guareschi's method, obtaining a good yield of the substance $C_5H_{10} > C < \begin{smallmatrix} CH(CN) \cdot CO \\ CH(CN) \cdot CO \end{smallmatrix} > NH$. The existence of the $\alpha\beta$ - or conjugated form in the liquid ester is also proved by a comparison of its optical properties with those of its methyl derivative, in which the $\beta\gamma$ -form alone is possible.

The existence of the $\beta\gamma$ -form is more difficult to prove, but we think that the great readiness with which the substance forms a sodio-derivative and undergoes alkylation points quite definitely to the existence of such a phase. The production of the $\beta\gamma$ -phase is, as has been explained, favoured by the presence of the cyclohexane ring, and therefore it is not surprising that ethyl α -cyanoheptylideneacetate, in which this factor is not present, does not react with α -bromoacetophenone: the tendency to form the doubly conjugated system $\cdot CHC(CN) \cdot C(OEt) \cdot O$ here is so great that the $\beta\gamma$ -phase is suppressed and the substance is no longer tautomeric (or tautomeric only to a small extent).

In order further to test the correctness of this interpretation, we have prepared the α -methyl derivative of ethyl α -cyanocyclohexylideneacetate and subjected it to the action of sodium ethoxide. We have found that owing to the great tendency to acquire a mobile hydrogen atom this compound readily loses ethyl carbonate, yielding α -cyclohexenylpropionitrile (compare Ingold and Thorpe, *ibid.*, 1919, **115**, 143). It is only reasonable to suppose that the $\beta\gamma$ -form of the nitrile is the first to be produced.



and that the hydrogen is then free to wander to the most stable position; we have not yet examined the nitrile in detail and therefore it is proposed to discuss its constitution in a further communication.

EXPERIMENTAL.

Synthesis of cyclohexenylacetone (III).—A solution of zinc methyl iodide was prepared by heating together 20.8 c.c. of methyl iodide, 10.8 c.c. of ethyl acetate, 25 c.c. of benzene, and 43 grams of zinc-copper couple,* a few crystals of iodine being added to start the reaction; the addition of the iodine can be omitted and the amount of zinc-copper couple reduced to 22 grams if the zinc copper couple residues from a previous operation are available. After boiling for one and a half hours under an efficient reflux condenser provided with a calcium chloride tube, the mixture was cooled in ice, the liquid decanted, and the solid residue washed two or three times with dry benzene, the washings being added to the benzene solution.

A benzene solution containing 20 grams of cyclohexylidenacetyl chloride (prepared by warming 21 grams of carefully purified cyclohexylidenacetic acid with 20 c.c. of thionyl chloride for half an hour and distilling the mixture under reduced pressure: the acid chloride boiled at $123^{\circ}/28$ mm.) was slowly run into the solution of zinc methyl iodide with constant cooling and shaking. The mixture was left in the freezing mixture for half an hour, then at the ordinary temperature for about an hour, before adding ice and ice-cold 10 per cent. sulphuric acid. After thorough shaking, the aqueous layer was extracted with ether, and the ether added to the benzene solution; this was washed successively with water, aqueous sodium hydrogen carbonate containing sodium thiosulphate, and three times with a saturated aqueous solution of ammonium sulphate, and then filtered, dried, and the ether and benzene distilled off, a long fractionating column being used to prevent loss of ketone. The residue was fractionated at atmospheric pressure, 10.5 grams being collected between 200° and 220° ; the fractions 180° – 200° and 220° – 260° weighed collectively about 4 grams and gave an abundant precipitate when treated with semicarbazide acetate. The main fraction was redistilled under reduced pressure and the middle fraction obtained was found to possess the following physical properties: d_4^{25} 0.93711; n_D^{25} 1.47251, whence $[R_L]_D$ 41.31, in very good agreement with values previously found for cyclohexenylacetone.

The whole quantity of ketone was then converted into the

* This was prepared by heating molecular quantities of finely ground copper oxide and zinc dust in a stream of dry hydrogen at about 200° .

semicarbazone, which was precipitated in its usual caseous form. Having been dried, and ground with light petroleum, the semicarbazone was triturated with dry ether (compare Wallach, *loc. cit.*), and the residue crystallised from methyl alcohol. The purification of the semicarbazone is an extremely tedious operation owing to the presence, apparently in small quantity, of a second substance of very similar properties, from which it can only be separated after a considerable number of crystallisations: this also applies to cyclohexenylacetonesemicarbazone obtained by other methods. When pure, the semicarbazone melted at 145° and was in every way identical with a sample prepared by Wallach's method.

We have succeeded in isolating a small amount of a second substance (see above) the presence of which appears to cause the difficulty experienced in purifying the semicarbazone. This substance proved to be an isomeric *semicarbazone*, which crystallised from benzene in small, lustrous plates melting at 169° (Found: C = 61.19; H = 9.11. $C_{10}H_{17}ON_3$ requires C = 61.51; H = 8.77 per cent.). The quantity obtained up to the present is not sufficient to establish its constitution, but it may possibly be the semicarbazone of cyclohexylideneacetone. It differs from the substance melting at 145° by the fact that it does not lose its lustre on exposure to the air, whilst the latter becomes powdery and opaque after a few days.

The soluble substance extracted by ether which Wallach found to melt at 137° appears to be a mixture of the new substance, m. p. 169° , with the ordinary form melting at 145° , as on repeated crystallisation the melting point gradually rises to 145° and the product is found to be identical with the ordinary form, m. p. 145° .

The preparation of cyclohexenylacetone was also carried out, using Δ^1 -cyclohexeneacetic acid as starting material. The chloride of this acid boiled at $109^{\circ}/29$ mm., and gave on treatment with zinc methyl iodide a somewhat smaller yield of cyclohexenylacetone than its isomeride. The identity of the ketone with cyclohexenylacetone was confirmed by the formation of the semicarbazone melting at 145° and also by the ready condensation with ethyl sodiomalonate under the conditions described by Norris and Thorpe (*loc. cit.*), a good yield of the resorcinol derivative being obtained: this was found to have the correct melting point after crystallisation from dilute alcohol.

Examination of the Acid Chloride Used.—In order to make certain that no displacement of the double bond had occurred when cyclohexylidene- and Δ^1 -cyclohexeneacetic acids were converted into the respective acid chlorides, test portions of these chlorides were reconverted into the acids by means of dilute aqueous sodium

carbonate. The acids precipitated on acidifying the alkaline liquid showed a correct melting point and solidified at once. The two ethyl esters were also prepared by treating the acid chlorides with ethyl alcohol. Ethyl *cyclohexylideneacetate* had b. p. $110^{\circ}/12$ mm., $d_4^{19.5}$ 0.98500, $n_D^{19.5}$ 1.47849, whence $[R_L]_D$ 48.36; and ethyl Δ^1 -*cyclohexeneacetate* had b. p. $104^{\circ}/18$ mm., $d_4^{19.5}$ 0.98138, $n_D^{19.5}$ 1.46410, whence $[R_L]_D$ 47.28 (compare Auwers and Ellinger, *Annalen*, 1912, 387, 200).

Transformation of Ethyl cycloHexylideneacetate into Ethyl Δ^1 -cycloHexeneacetate.—Thirty grams of ethyl *cyclohexylideneacetate* (b. p. $120^{\circ}/35$ mm.; $[R_L]_D$ 48.67), 60 grams of potassium hydrogen sulphate, and 2 grams of water were heated for three hours at 160° under reflux; after addition of more water, the esters were isolated by distillation in a current of steam, and extracted from the distillate with ether. The ethereal solution was dried and the solvent removed with the aid of a column; the residue was then distilled under reduced pressure, when the whole passed over at 110 – $120^{\circ}/18$ mm. The molecular refraction of the distillate was determined: $[R_L]_D$ = 48.03, indicating a conversion to the extent of about 50 per cent.

Ethylation of cycloHexenylacetone.—*cycloHexenylacetone* (13.8 grams) was added to a cooled solution containing 2.3 grams of sodium in 30 c.c. of ethyl alcohol. To the orange-red solution an excess of ethyl iodide was added and the whole heated under reflux for about three hours, when it was found to be nearly neutral. The ketone was isolated by adding water and extracting with ether; after drying, the ethereal solution was evaporated and the ketone fractionated, the portion boiling above 180° being treated with semicarbazide in the usual way. The semicarbazone formed separated in crops, the first crop being crystalline and representing a yield of about 30 per cent. of a new compound, which crystallised well from ethyl alcohol in fine, sparkling plates melting at 185° ; the subsequent crops contained mainly the semicarbazone of *cyclohexenylacetone* and only very little of the new compound. It must be mentioned that methyl alcohol does not effect a good separation.

The substance melting at 185° is the *semicarbazone* of α -ethyl- Δ^1 -*cyclohexenylacetone* (VII) (Found: C = 64.31; H = 9.58. $C_{12}H_{21}ON_2$ requires C = 64.43; H = 9.49 per cent.). The *ketone*, regenerated from it in the usual manner by means of oxalic acid, showed the following properties: b. p. 221 – 263 mm. (thermometer in the vapour up to 100°), $d_4^{20.4}$ 0.9181, $n_D^{20.4}$ 1.46926, whence $[R_L]_D$ 50.42 (calc., 50.34) (Found: C = 79.12; H = 10.95. $C_{11}H_{18}O$ requires C = 79.47; H = 10.90 per cent.). The odour of the ketone is reminiscent of that of *cyclohexenylacetone* and cedarwood oil.

Synthesis of α -Ethyl- Δ^1 -cyclohexenylacetone.—The synthesis of the ketone was carried out, using α -ethylcyclohexeneacetic acid, prepared according to the method of Wallach (*Annalen*, 1908, **360**, 44), as the starting material. The acid chloride obtained was found to boil at $120^\circ/28$ mm.; 41 grams of this substance were treated with an excess of zinc methyl iodide as described on p. 1370, and 22 grams of a liquid boiling between 210° and 250° were obtained in addition to small fractions of high and of low b. p. All these fractions were treated with semicarbazide acetate, and 18 grams of semicarbazone collected. After one crystallisation from alcohol, the semicarbazone melted at 185° and did not depress the melting point of the substance obtained from the ethylation of cyclohexenylacetone.

The ketone regenerated from it boiled at 221° and had d_{40}^{20} 0.91976, n_D^{20} 1.47005, whence $[R_L]_D$ 50.40; its identity with the ketone produced by the direct ethylation of cyclohexenylacetone is therefore established.

Synthesis of $\alpha\alpha$ -Dimethyl- Δ^1 -cyclohexenylacetone (V).—This was carried out precisely as in the case of the isomeric ethyl compound, the starting material being Δ^1 -cyclohexenylisobutyric acid (Wallach, *loc. cit.*).

The ketone was obtained in the form of its semicarbazone, which forms tufts of long, silky needles melting at 150 – 151° after crystallisation from dilute methyl alcohol. The ketone boiled at $221^\circ/765$ mm. (thermometer in the vapour up to 80°) and had d_{40}^{20} 0.93288, n_D^{20} 1.47565; whence $[R_L]_D$ 50.20 (calc., 50.34) (Found: C = 79.53; H = 10.87. $C_{11}H_{18}O$ requires C = 79.47; H = 10.90 per cent.).

The ketone is a colourless oil with a strong camphoraceous odour, somewhat reminiscent of that of the ethyl isomeride.

Experiments on Ethyl α -Cyanocyclohexylideneacetate and its Methyl Derivative.—The ester was prepared by the method of Harding, Haworth, and Perkin (*loc. cit.*), using piperidine as a condensing agent.

A specimen of the ester, purified by two distillations under reduced pressure (b. p. $151^\circ/10$ mm.), gave d_{40}^{20} 1.05394, n_D^{20} 1.49670, whence $[R_L]_D$ 53.94, the calculated value being 51.59.

The ester (19.3 grams) was treated with ethyl cyanacetate (11.3 grams) and ethyl-alcoholic ammonia (saturated at 0° , 75 c.c.) for twelve hours. The product solidified and on working up in the usual way (Kon. T., 1921, **119**, 810) 15 grams of the ω -imide of $\alpha\alpha'$ -dicyanocyclohexane-1:1-diacetic acid were obtained, the identity of the substance being established by comparison with a genuine specimen.

Ethyl α -cyano- α -methyl- Δ^1 -cyclohexeneacetate (p. 1368) was pre-

pared by the method of Harding, Haworth, and Perkin, the methylation being repeated to ensure that none of the parent material remained unchanged. The ester boiled very constantly at $133^{\circ}/9$ mm. and had $d_{4}^{20.0}$ 1.04776, $n_{D}^{20.0}$ 1.47819; whence $[R_D]_D$ 55.98 (calc., 56.21).

From a comparison of the molecular refractivity of the methyl compound with that of the parent substance it is clear that the latter must possess a system of conjugated double bonds which causes the very considerable exaltation observed.

Action of Sodium Ethoxide on Ethyl α -Cyano- Δ^1 -cyclohexenepropionate.—The ester (15 grams) was mixed with a solution of sodium (23 grams) in ethyl alcohol (30 c.c.) and kept at 35° for four hours. Water was then added and the precipitated oil, which had the odour of ethyl carbonate, was isolated with ether. A portion boiled below $80^{\circ}/30$ mm., and at $126^{\circ}/765$ mm. on redistillation, and had the usual properties of ethyl carbonate. The remainder boiled at $120^{\circ}/30$ mm. and consisted of pure Δ^1 -cyclohexenepropionitrile (Found: N = 10.69. Calc., N = 10.35 per cent.). No fraction of higher b. p. was obtained, showing that the elimination of the carbethoxyl group had been quantitative.

In conclusion, our thanks are due to Professor J. F. Thorpe, F.R.S., for his kind interest in the progress of this investigation.

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(Received, March 11th, 1921.)

CLX.—Binary Critical Solution Temperatures as Criteria of the Purity of Acetic Acid.

By DAVID CHARLES JONES.

CRISMER (*Bull. Soc. chim. Belg.*, 1895, **9**, 145; 1896, **10**, 312; 1904, **18**, 1; 1906, **20**, 294) first demonstrated, in the well-known system ethyl alcohol-petroleum, the extreme sensitiveness of a binary critical solution temperature to certain impurities. Thus the presence of 1 per cent. of water in the alcohol raised the critical solution temperature by 17° . Since that time, a considerable number of such systems have been investigated (Timmermans *Z. physikal. Chem.*, 1907, **58**, 129), but apart from investigations actually dealing with these phenomena, their use as criteria of purity has been very largely neglected (*vide*, however, Orton and Jones, *T.*, 1919, **115**, 1056; Tizard and Marshall, *J. Soc. Chem. Ind.*, 1921, **40**, 207). The number of such systems available for this

purpose is limited. A study of the solubility of organic liquids reveals how comparatively rare a critical solution must be at the ordinary temperature and pressure. In the fatty acid series, formic acid gives with benzene a binary critical solution temperature at 73.2° (Ewins, T., 1914, **105**, 350). On the other hand, anhydrous formic acid is completely miscible with phenetole and the other ethers of this series which are similar to benzene in solubility relations. One of the higher ethers of this series is the only material we know with which formic acid may form a critical solution at the ordinary temperature and pressure. Thus formic acid, containing about 2 per cent. of water and melting at 4.2° , forms a critical solution with *o*-tolyl methyl ether at about 30° . The same acid, whilst being completely miscible with phenyl *n*-butyl ether, forms a critical solution above its boiling point with benzyl *n*-butyl ether. Propionic acid has no known solubility relations. *n*-Butyric acid is completely miscible with the higher paraffins, but is only partly so with water, the critical solution temperature being -37° (Rothmund, *Z. physikal. Chem.*, 1908, **63**, 57).

The fact that the great majority of organic liquids are either completely miscible, or so immiscible as to render the determination of critical solution temperatures impracticable, suggested the research on ternary critical solution temperatures which is described in the following paper.

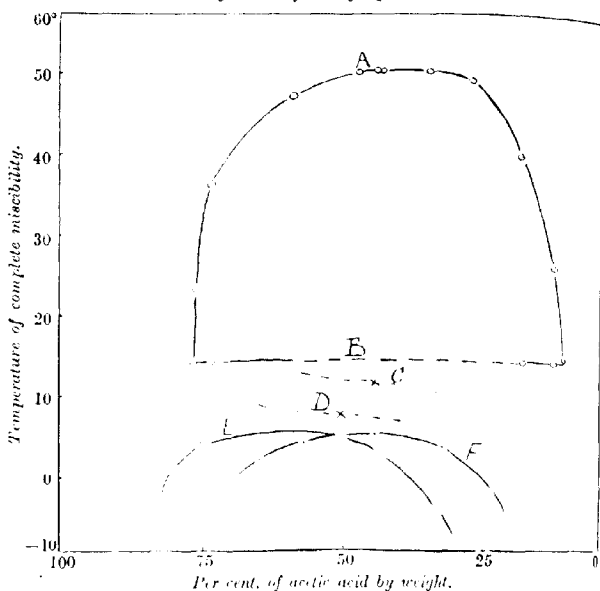
The binary critical solution temperatures of the following substances are well established: these would seem to be valuable additions to the ordinary criteria of purity, and are, in general, far more sensitive than other physical properties such as density, refractive index, or boiling point: ethyl alcohol and petroleum (Crismer, *loc. cit.*); methyl alcohol and carbon disulphide (Rothmund, *loc. cit.*); phenol and water (Timmermans, *loc. cit.*); hexane and nitrobenzene (Timmermans, *loc. cit.*); formic acid and benzene (Ewins, *loc. cit.*); *n*- and *isobutyric* acid and water (Rothmund, *loc. cit.*); aniline and hydrocarbons (Tizard and Marshall, *loc. cit.*). A complete list (up to 1918) of binary critical solution temperatures will be found in Roozeboom's "Das Heterogene Gleichgewicht," II, 2, p. 70, etc.

The complete solubility curve of acetic acid and a petroleum fraction (b. p. 185° – 195°), and the effect of water present in the acetic acid on its critical solution temperature, are described here. It has also been found that anhydrous acetic acid forms metastable mixtures with cyclohexane and with carbon disulphide, the partial miscibility of which is extremely sensitive to water present as an impurity in the acetic acid.

Fig. 1 represents the solubility curves obtained in the binary

systems acetic acid-petroleum, carbon disulphide-acetic acid, and cyclohexane-acetic acid, by plotting concentration against temperature. The curves have the normal round-topped form, the same temperature of solution being obtained in the neighbourhood of the critical point although the composition may vary by several units per cent. In the petroleum-acetic acid system, the curve

FIG. 1.
Solubility curves of binary liquid mixtures.



A, Acetic acid-petroleum; B, freezing-point curve of acetic acid-petroleum; C, freezing-point curve of acetic acid-cyclohexane, approx. indicated; D, freezing-point curve of acetic acid-carbon disulphide, approx. indicated; E, acetic acid-carbon disulphide; F, acetic acid-cyclohexane.

is cut at 14° by the solidification curve when there is 9 per cent. of petroleum in the lower layer and 24 per cent. of acetic acid in the upper layer. These figures of course represent the solubility of acetic acid in petroleum, and of petroleum in acetic acid at this temperature. As has been already noted, in the other two cases the solidification curve lies well above the partial miscibility curve. Thus, in the case of cyclohexane with a critical solution temperature at 4.2° , the melting point, with these same critical proportions

present, is 11° , and in the case of carbon disulphide, with practically critical proportions, the saturation point is 3.9° and the melting point 7.8° .

The acid used in the investigation of the system acetic acid-petroleum melted at 16.5° . In the other two cases, a large quantity of purified acid, melting at 16.4° , was redistilled in the closed, all-glass apparatus mentioned later, and the large fraction obtained, melting at 16.58° , was used in determining the temperature of miscibility. The impurity was probably water, the quantity present in the acid melting at 16.58° being less than 0.05 per cent., and in the acid melting at 16.5° less than 0.1 per cent.

It is interesting to observe that carbon disulphide and cyclohexane have practically the same critical solution temperature. They afford very clear illustrations of that type of liquid system in which no stable miscibility curves exist owing to the incidence of the melting-point curves, that is, both carbon disulphide and cyclohexane are ordinarily spoken of as completely miscible with acetic acid. The results given here show that the partial liquid solubility curves lie hidden just underneath the melting-point curve (*vide* "Das Heterogene Gleichgewicht," II, 2, p. 129). Undoubtedly if a series of curves was obtained from mixtures of carbon disulphide, cyclohexane, and the lower petroleum (hexane), up to the petroleum fraction used in this paper, with anhydrous acetic acid, one would obtain results showing the gradual shifting of the partial liquid miscibility curves from the metastable region below the melting-point curve into the stable region above this curve. The melting-point curve also rises as greater insolubility occurs, but only, of course, to a much slighter extent.

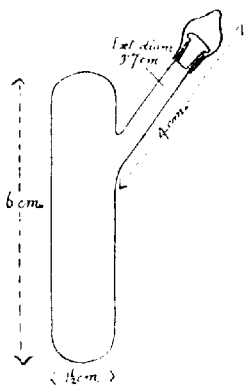
As is more fully described in the following paper, the effect of water is to decrease markedly the mutual solubility of these systems. Thus the presence of so small a quantity of water as 0.9 per cent. in the acetic acid raises the whole solubility curve of cyclohexane-acetic acid well above the melting-point curve (*vide* Fig. 1, following paper). On the other hand, acetic acid must contain from 8–9 per cent. of water to bring the partial miscibility curve of acetic acid-toluene into view, and approximately 16 per cent. of water in the case of acetic acid-nitrobenzene. The discovery of the metastable critical solution temperature in the cases of cyclohexane and carbon disulphide with acetic acid thus gives confirmation of the views Finstermans has brought forward in other cases. Although it may be incorrect, therefore, to draw conclusions regarding the solubility of toluene in anhydrous acetic acid from the behaviour of the system toluene-acetic acid-water (8 per cent.) and thus compare the "solubility" of toluene in acetic acid with, say, that of cyclo-

hexane in acetic acid, which latter system requires only a few tenths of 1 per cent. of water to give partial miscibility relations, yet certainly a prediction from this last fact that the miscibility curve of *cyclohexane*-acetic acid should lie slightly below the melting-point curve is confirmed by the presence of the metastable curve ("Das Heterogene Gleichgewicht," II, 2, p. 134).

EXPERIMENTAL.

The ordinary synthetic method of determining points on the solubility curves was used, that is, mixtures were made up by weight, and the temperature of disappearance of the two layers was noted. It being very essential to avoid access of moisture, the materials were introduced into a small glass tube, closed except for a narrow side arm of very thin glass, attached near the top of the tube at an angle of about 30° , through which a tiny pipette containing the liquids could be introduced. In the case of the petroleum-acetic acid mixtures, with their higher miscibility temperatures, the side arm was sealed off, but in the other systems it was found very convenient to close the side arm by means of ground-in double stoppers of the type used in ordinary ether bottles (Fig. 2). The thermometers, of the Anschütz type, standardised by the Bureau of Standards, were attached externally to the tube by a rubber band. This was the type of apparatus also used in the following paper for the determination of ternary critical solution temperatures.

FIG. 2.



Critical Phenomena.

It is remarkable that with petroleum-acetic acid the ordinary phenomena observed in such cases are almost entirely absent. Some degrees below the critical solution temperature, the surface of separation between the two layers requires attentive observation to be seen at all, owing, presumably, to the very slight difference of refractive index. At temperatures below, but in the immediate neighbourhood of, the critical solution temperature, the surface of separation is extremely difficult to detect. In this region also, very rapid separation of the layers occurs after shaking, due, it is

supposed, to the wide difference of density of the two components, so that the fairly stable emulsion usually formed in this region is absent, and when temporarily produced by vigorous shaking it is non-opalescent owing to the slight difference of refractive index. Immediately above the critical solution temperature there is observed just the merest trace of the usual critical opalescence. The similarity of refractive index of the components would account for this (*vide* Smoluchowski, *Ann. Physik*, 1908, **25**, 205; Einstein, *ibid.*, 1910, **33**, 1275).

In the case of *cyclohexane* and acetic acid, the phenomena are more pronounced although still very slight, but in the carbon disulphide-acetic acid system very marked and beautiful phenomena are displayed, permanent emulsions which are strongly opalescent being formed below and near the critical solution temperature, corresponding, apparently, to the greater difference of refractive index and similarity in density between the phases in this system; the critical opalescence above the critical solution temperature is very intense.

Preparation of Materials.

The acetic acid was originally a specimen of high purity having m. p. 16.0° . Large quantities were fractionated through a 6-column Young evaporator still-head in an all-glass apparatus and there were obtained finally about 1,500 c.c. of material, m. p. 16.45° . On distillation of this material through the same apparatus, large middle and final fractions were obtained melting at 16.58° , the first fraction of about 200 c.c. having m. p. 16.40° , and containing most of the water present as impurity.

To obtain the petroleum, purified kerosene was fractionated through a 4-bulb still-head and the portion boiling from $180-200^{\circ}$ was collected. This was shaken with 95 per cent. sulphuric acid (which removes the olefines, Colman and Yeoman, *J. Soc. Chem. Ind.*, 1919, **38**, 57T; Thole, *ibid.*, 39T), until a fresh portion of acid remained uncoloured. The hydrocarbon was then heated under reflux for several days with a mixture of nitric and sulphuric acids to remove the aromatic compounds. After further prolonged treatment with sulphuric acid, it was finally shaken with silica gel, which effectively removed any acid left in suspension or solution and dried the petroleum. In the final distillation, a fraction boiling at $185-195^{\circ}$ was obtained: this was the petroleum used.

The purification of the carbon disulphide is described in the following paper.

The *cyclohexane* was prepared synthetically from benzene and purified by repeated sulphonation, followed finally by fractional crystallisation. The material used melted at 6.4° .

Effect of Water Present in the Acetic Acid.

Pipettes of the kind previously described (Orton and Jones, T., 1919, **115**, 1064) were graduated to deliver the critical proportions of acetic acid and the other component, petroleum, carbon disulphide, or cyclohexane. The acetic acid pipette had a capacity of 0.5824 c.c., and the pipettes used for the other component a capacity of 0.4959 c.c. in the case of carbon disulphide, and 0.6483 c.c. in the cases of cyclohexane and petroleum. Acetic acid of various strengths was made up by diluting 250 c.c. of the pure acid with distilled water. The melting point of the acid was taken with a Beckmann thermometer, standardised by means of an accurate Anschütz thermometer.

The mixture was warmed to 20° and the critical solution temperatures were taken immediately. The Beckmann thermometer remained in the liquid. The pipettes for the introduction of water or for the removal of acetic acid for estimation, were inserted through a tiny tube sealed in the ground-glass stopper. Every precaution had to be taken to avoid the incursion of moisture. The same experimental tubes were used as before described, and these had to be carefully dried, and were always kept ready for use over sulphuric acid in a desiccator.

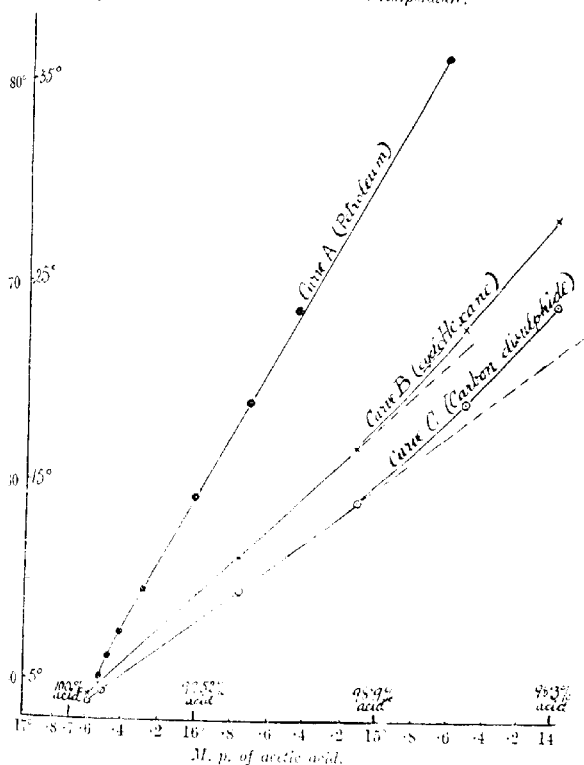
Fig. 3, curve A, shows the rather remarkable character of the results obtained. The presence of water in the acetic acid raises the critical solution temperature almost linearly. In the petroleum-acetic acid system, the curve seems to be quite linear between the points corresponding to acids of m. p.'s 16.4° and 14.6°. In this region, a difference of 1° in the melting point corresponds to a difference of 16° in the critical solution temperature. In the case of an acid melting at 16.4-16.5°, a slight bend in the curve is evident, and here a difference of 1° in the melting point corresponds to a difference of 20° in the critical solution temperature. Thus for the main portion of the curve the presence of 1 per cent. of water in the acetic acid raises the critical solution temperature by about 32° with this petroleum. It is clear that the curve cannot remain linear for any considerable percentage of water, since, if this were so, the miscibility temperature of water and petroleum when water has completely replaced the acetic acid would be impossibly high.

It is obvious that traces of water could be measured in this way, since the temperature can be easily read to an accuracy of 0.02°. Owing, however, to the difficulty of keeping out slight traces of water, and to the fact that the accuracy of the pipettes is limited, a critical solution temperature of this type can be relied on only

to 0.05° . The large effects observed are, of course, due to the great difference of solubility of water in acetic acid and in petroleum, affording certainly the most striking instance yet discovered of the extreme sensitiveness of critical solution temperatures to certain impurities.

FIG. 3.

Effect of water on the critical solution temperature.



It was evident, however, that it would be very difficult to duplicate exactly the petroleum fraction, and that the use of a liquid of definite purity would have been preferable in this work, and of considerable value in fixing definitely an independent criterion of purity. The work that is described in the following paper has shown that when the acetic acid contained 0.6 per cent. of water,

that is, melted at 15.3° , cyclohexane and carbon disulphide gave critical solution temperatures at 15° and 12.4° , respectively. Considering the immense effect of water on the critical solution temperature of the acetic acid-petroleum binary mixture, and the position of the melting-point curves of the former systems, it was thought very improbable that anhydrous acetic acid would give partial miscibility relations with these materials. It was found, however, that in both cases marked supercooling could occur, quite considerable regions separating the stable and metastable melting-point curves, which made it possible in both cases to realise the metastable partial miscibility curves. The binary curves with an acetic acid melting at 16.58° have already been given.

In Fig. 3, curves *B* (cyclohexane) and *C* (carbon disulphide) illustrate the effect of water in the acid on the value of the critical solution temperature. In both cases, as would be expected, the effects are considerably less than in the case of petroleum, being slightly greater in the case of cyclohexane. From Fig. 3, it appears that the proportions used in the carbon disulphide-acetic acid system were not quite critical, containing too little of the former. This may account for the low values obtained in this case.

In the linear portions of the curves for cyclohexane and carbon disulphide, a difference of 1° in the melting point of the acid corresponds to a difference of 8.4 and 6.9, respectively, in the critical solution temperature. The deviation of the curves from linearity is probably due to the more rapidly decreasing sensitiveness of the melting point to the presence of water in the acid (*vide* Faueon's results, *loc. cit.*, for the lowering of the melting point of acetic acid by water). If the change of sensitiveness were the same for the melting point as for the critical solution temperature, the above curves would be sensibly linear. This probably accounts for the linear character of curve *A*, the critical solution temperatures in the petroleum-acetic acid system decreasing in sensitiveness more rapidly than in the other two systems, with increasing water content.

In general, the critical solution temperatures of concentrated acetic acid and carbon disulphide or cyclohexane provide very sensitive independent methods for the estimation of the water content. The ease of purification of carbon disulphide and cyclohexane should make the method generally useful in this connexion.

On the other hand, the critical solution temperatures obtained with a petroleum of about the boiling point given, purified from unsaturated and aromatic hydrocarbons, are about twice as sensitive to traces of water; and once a given petroleum has been standardised against an acetic acid the water content of which has been determined accurately either by means of the other two critical solution

temperatures already obtained, or by an accurate determination of the melting point, it would provide an extraordinarily delicate method of estimating changes in the concentration of water in acetic acid.

Results (vide Fig. 1).

Petroleum acetic acid.

% Acetic acid.	Miscibility temp.	% Acetic acid.	Miscibility temp.
24.54	22.90	56.96	59.15*
26.92	36.20	65.57	50.50*
41.00	47.20	73.50	48.90
52.72	49.85	82.51	39.60
56.91	50.15	88.51	25.6

cycloHexane-acetic acid.

% Acetic acid.	Miscibility temp.	% Acetic acid.	Miscibility temp.
34.5	1.4	67.03	2.8?
42.3	3.2	76.0	-2.8
54.6	4.2*		

Carbon disulphide-acetic acid.

% Acetic acid.	Miscibility temp.	% Acetic acid.	Miscibility temp.
19.6	0.5?	24.6	2.6?
42.7	3.9*	49.3	3.9
56.1	2.0	66.1	-5.2

* Critical proportions.

Results (vide Fig. 3).

Effect of water on the petroleum acetic acid binary mixture (Curve A).

The acetic acid (99.9%) melted at 16.50.

M. p. of acetic acid.	C.S.T.	M. p. of acetic acid.	C.S.T.
16.5?	50.15	15.69	63.8?
16.39	52.4	15.44	68.5
16.26	54.5	14.6	81.1
15.98	59.15	16.46	51.2

Effect of water on the cyclohexane-acetic acid binary mixture (Curve B).

The acid (99.94%) melted at 16.58.

M. p. of acetic acid.	C.S.T.	M. p. of acetic acid.	C.S.T.
16.53?	4.75	14.5	22.62?
15.75	11.1	13.98	28.2
15.12	16.6	16.58	4.2

*Effect of water on the carbon disulphide-acetic acid binary mixture (Curve C).*The acid (99.94₀) melted at 16.58°.

M. p. of acetic acid.	C.S.T.	M. p. of acetic acid.	C.S.T.
16.5°	4.4°	14.5°	18.9°
15.57	9.4	13.98	23.92
15.12	13.9	16.58	3.9

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[Received, November 2nd, 1922.]

CLXI.—Ternary Critical Solution Temperatures as Criteria of Liquid Purity.

By DAVID CHARLES JONES.

THE critical solution temperatures observed in the three component systems toluene-acetic acid-water and *n*-butyl alcohol-hydrogen chloride-water were investigated by Orton and Jones (T., 1919, **115**, 1055, 1194) as criteria of the purity of toluene and *n*-butyl alcohol. It had been thought previously that owing to the necessity for the exact adjustment of the concentration of the three components of the system, ternary critical solution temperatures would not be available as exact criteria of purity. Although theoretically both in the case of binary and ternary systems, the concentrations must be defined in order to obtain an invariant point at constant pressure, it is found experimentally that the binary solubility curve is flat-topped, and therefore the temperature of miscibility is the same through a considerable range of concentration of the components in the neighbourhood of the critical solution temperature. On the other hand, ternary critical curves in this same region sometimes pass through very considerable ranges of temperature for slight changes of concentration, the eventuality depending wholly on the nature of the components, just as, in a binary system, an impurity (third component) may or may not produce a large effect on the critical solution temperature.

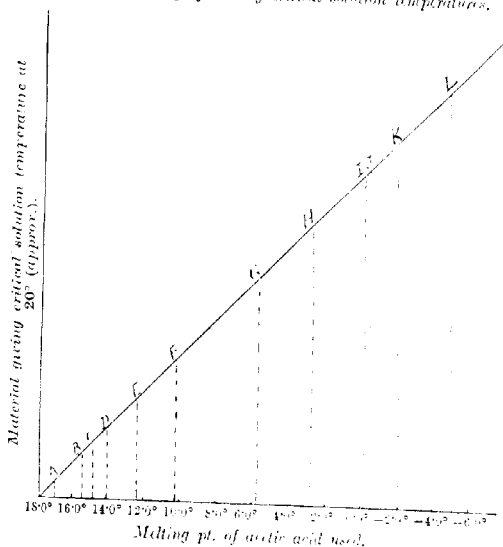
The use of accurate pipettes, one for the solution, and another for the liquid the purity of which is to be tested, overcomes this difficulty even in the case of very sensitive critical solution temperatures, and such pipettes should be used even for the determination of binary critical solution temperatures, because the system is really ternary if an impurity is present.

In other respects, ternary critical solution temperatures have the same advantages as binary. The critical solution phenomena

are in general very beautiful and distinct, thus making the point of final disappearance of the striations very easy to detect. The whole determination is easily and rapidly made, and two advantages are secured; by suitably selecting two of the components and adjusting their concentrations, it is possible (1) to apply the method to a very large number of organic liquids, (2) to bring the

FIG. 1.

Graphical summary of ternary critical solution temperatures.



A, Petroleum (b.p. 150 approx.); B, gasoline (b.p. 80 approx.); C, cyclohexane; D, carbon disulphide; E, bromonitrobenzene; F, carbon tetrachloride; G, xylene; H, toluene; I, benzene; J, thiophene; K, phenol; L, nitrobenzene and related compounds.

miscibility point within any convenient temperature range at atmospheric pressure.

Acetic acid diluted with varying proportions of water is used in these experiments as the solutions, and by means of these the purity of a whole series of organic liquids is tested. As will be shown later, the higher petroleum form binary critical solutions with anhydrous acetic acid. Nearly all other simple organic compounds are soluble in acetic acid and only partly soluble in water, and increasingly dilute acid solutions are necessary to obtain the ternary critical solution temperatures. The method can thus

be used for all stable organic liquids except in the few cases where they are miscible with both acetic acid and water. In order to use this purity test, it is only necessary to establish first the approximate strength of the acetic acid, and secondly the proportion of solution to material the purity of which is to be tested, in order to obtain the miscibility point in the critical region. Having determined this, it is necessary to construct the accurate pipettes before mentioned, and thus to fix always the concentration in the system.

It is an important practical fact that in the series of organic liquids examined, the acetic acid solutions varying from 84 per cent. to the anhydrous acid, the critical proportions by volume vary only slightly in the direction of a smaller proportion of acid, so that the same pipettes can be used for cyclohexane and 99 per cent. acetic acid as for nitrobenzene and 84 per cent. acetic acid. If these proportions are adhered to, one gets throughout this range beautiful and clear critical phenomena.

In Fig. 1, the melting point of the acetic acid (for corresponding concentrations *vide* Faucon, *Ann. Chim. Phys.*, 1910, [viii], 19, 84) is given which, if used as solution, will give a clear critical solution temperature at about 20° with the organic material found at the corresponding ordinate, provided the solution and material are used in the proportion 0.5824 c.c. of acetic acid solution to 0.4959 c.c. of organic liquid. This applies, not only to the simple compounds indicated as ordinates, but also to a considerable number of their substituted derivatives. When these proportions are varied considerably the miscibility points are still in the critical region, and therefore give a clearly defined point, but of course at different temperatures.

Solubility Relations in the Systems Acetic Acid-cyclohexane, Acetic Acid-Nitrobenzene, and Acetic Acid p-Nitrotoluene.

cyclohexane, as has already been stated (preceding paper), has a binary metastable critical solution temperature at 42° . Fig. 2 shows graphically the solubility curves obtained when the acetic acid contains small quantities of water. *A* is the binary solubility curve with pure acid melting at 16.58° . *B* is the solubility curve obtained with an acid melting at 16.28° . *C* is the solubility curve obtained with an acid melting at 14.8° . The melting points 16.28° and 14.8° indicate the presence of 0.28 per cent. and 1.2 per cent. of water, respectively. The miscibility temperatures were obtained synthetically as before.

These curves bring out very clearly the remarkable effect of the presence of less than 1 per cent. of water on the form of the solubility curve. The points marked K_B and K_C on the curves *B* and *C* are

still the critical points for this system, giving clear critical phenomena, but owing to the water distributing itself so predominantly in the acid phase, strongly marked maximal points appear on the curves.

FIG. 2.
Solubility Curves.

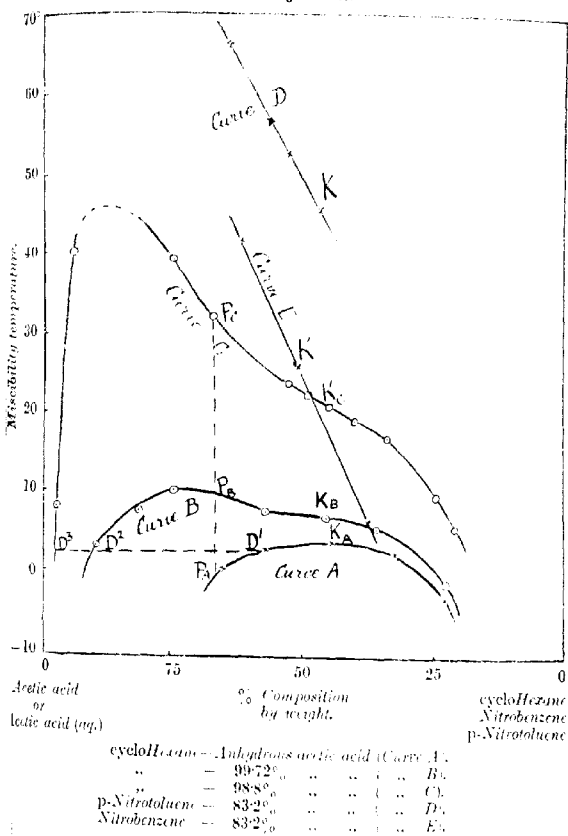


Fig. 2 also shows similar curves drawn through the critical regions for nitrobenzene and *p*-nitrotoluene with acetic acid containing about 16 per cent. of water. These curves bring out very clearly the difference in the form of the curves for binary systems,

ternary systems (with a large proportion of all three constituents), and a ternary system where one component is present in small quantity as an impurity. Thus in the "binary" system acetic acid-petroleum, in the direct neighbourhood of the critical solution temperature, there is no change in the temperature of miscibility whilst the composition changes from 50 to 70 per cent. of acetic acid. In the same composition range, the carbon disulphide-acetic acid and the cyclohexane-acetic acid systems show very slight changes. In the system cyclohexane-99 per cent. acetic acid, for a change of composition from 50 to 60 per cent., in the immediate neighbourhood of the critical solution temperature, the temperature change is 3.5° . In the nitrobenzene-aqueous acetic acid system, temperature changes of 14° occur for a change in composition from 50 to 60 per cent. acetic acid.

In systems showing marked maximal points, as in this case, far bigger changes in the miscibility temperature, for a certain percentage of impurity, can be obtained if proportions of constituents are chosen outside the critical region nearer to the maximal temperature. Thus from curves *A* and *C*, approximately 1 per cent. of water in the acetic acid produces a rise of 17° from K_A to K_C . If proportions represented by P_A and P_C are used, the same percentage of water in the acetic acid produces a rise in the miscibility temperature of about 31° . In this case, a change of proportions of this order still leaves the system sufficiently near to the critical region that accuracy is not sacrificed in the determination, but if the deviation from the critical proportions is too great the accuracy will be diminished markedly, owing to the difficulty of observation. The advantage obtained by changing proportions in this way obviously decreases as the concentration of the impurity increases. Thus from P_A to P_B there is a rise of about 45° for 1 per cent. of water as an impurity. In the petroleum-acetic acid system, however, any marked deviation from the critical proportions makes observations very difficult.

The great effect of water may be very clearly traced in the diminution of the solubility of acetic acid in the layer rich in cyclohexane. Thus, drawing an isotherm cutting the three curves *A*, *B*, and *C* at D^1 , D^2 , and D^3 , it is seen that the percentage of acetic acid in the layer rich in cyclohexane decreases from 42.3 per cent. when the acetic acid is almost anhydrous, to 11.8 per cent. when the acetic acid contains about 0.2 per cent. of water, and further to 3.6 per cent. when the acetic acid contains about 1 per cent. of water. On the other hand, very slight changes in the percentage concentration of cyclohexane in the layer rich in acetic acid occur as a result of the presence of the water.

TABLE I.

*Results (vide Fig. 2).**Curve B. cycloHexane and 99.72% acid.*

% cycloHexane.	Miscibility temp.	% cycloHexane.	Miscibility temp.
22.95	2.5°	36.54	5.3°
45.3	6.65	56.0	7.2
73.6	10.0	80.0	7.0
88.2	3.0	92.0	below 7.0

Curve C. cycloHexane and 98.80% acid.

20.67	5.2	24.13	9.3
34.22	16.7	39.93	18.9
44.95	20.6	49.00	22.1
52.35	23.6	65.73	31.8
73.81	38.0	93.00	40.0
96.4	8.0		

Curve D. Nitrotoluene and 83.2% acid.

% Nitrotoluene.	Miscibility temp.	% Nitrotoluene.	Miscibility temp.
46.94	45.2°	56.14	56.6°
52.70	52.2	63.81	66.2

Curve E. Nitrobenzene and 83.2% acid.

% Nitrobenzene.	Miscibility temp.	% Nitrobenzene.	Miscibility temp.
51.05	25.5°	61.99	41.5°
57.54	6.3		

Nitrobenzene-Aqueous Acetic Acid.—Nitrobenzene has many excellent criteria of purity. The heat of fusion is small enough to make its melting point (5.9°) very sensitive to impurities, and it has a little known binary critical solution temperature with hexane at 19.2° (Timmermans, *Z. physikal. Chem.*, 1907, **58**, 129). For final purification, it was distilled under diminished pressure through a 6-column Young evaporator still-head, an all-glass apparatus. The following may be taken as typical of a final distillation, the critical solution temperature values being taken with an acetic acid melting at -5.4° , containing 83.2 per cent. of acetic acid.

	Volume in c.c.	M. p.	C.S.T.
1st fraction	150	5.4°	17.2°
2nd "	350	5.9	17.3
3rd "	150	5.8	17.3
4th "	200	5.8	17.38

The following table gives the critical solution temperatures of compounds closely related to nitrobenzene, the same acid and the same proportion of constituents being used.

TABLE II.

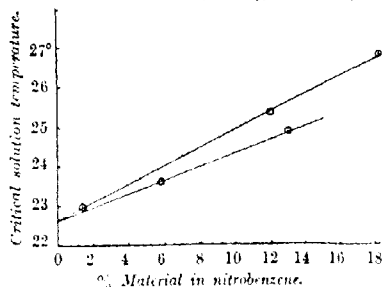
	C.S.T.		C.S.T.
Nitrobenzene.....	22.5°	<i>o</i> -Nitrotoluene	42.55°
<i>m</i> -Nitrotoluene	52.0	<i>p</i> -Nitrotoluene	46.0
<i>o</i> -Chloronitro- benzene	56.8	Bromomesitylene ...	2.0
		(with acid melting at 11.8°)	

TABLE III.

Results (vide Fig. 3: acid 83.2%).

% <i>p</i> -Nitro- toluene.	C.S.T.	% <i>m</i> -Dinitro- benzene.	C.S.T.
0	22.55°	0	22.55°
1.67	23.00	5.792	23.5
12.06	25.25	13.13	24.8
18.12	26.80		

FIG. 3.

Acid melts at -5.4° (\cong 83.2% acetic acid).

m-Dinitrobenzene, strangely enough, raises slightly the critical solution temperature of nitrobenzene, that is, the introduction of the second nitro-group seems to produce a solubility effect opposite in direction to that following the introduction of the first.

The influence of the methyl group appears to be the same in the case of benzene-toluene as in that of nitrobenzene-nitrotoluene, producing almost the same rise in the critical solution temperature (27° in the case of benzene-toluene, 20° for the *o*-nitro- and 29.5° for the *m*-nitro-derivatives).

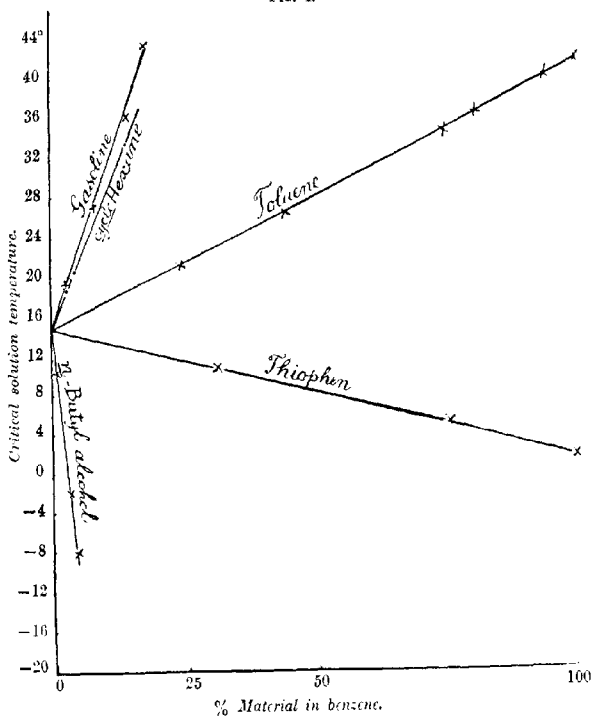
Benzene-Aqueous Acetic Acid.—The material, which originally had a melting point of 5.4°, was distilled through a 12-bulb still-head, and the following fractions, having the melting points and critical solution temperatures given below, were obtained:

	Volume in c.c.	M. p.	C.S.T.
1st fraction	20	5.4°	14.9°
2nd "	75	5.45	14.9
3rd "	7	5.4	15.0
Residue	12	5.2	15.8

The critical solution temperatures were taken using a solution of acetic acid melting at 0.9° , which corresponds to an 88.3 per cent. acid.

Fig. 4 shows the effect of certain typical impurities on the benzene critical solution temperature. Thiophen (synthetically prepared and carefully purified), when the same proportions and the same

FIG. 4.



acetic acid solutions are used as for benzene, exhibits a very clear critical solution temperature at 1.9° ; that is, thiophen is very similar to benzene in solubility relations, 1 per cent. of thiophen lowering the benzene critical solution temperatures by 0.13° only, and therefore this method would only estimate it in benzene to an accuracy of about 1 per cent. The toluene curve is included for completeness from a former paper (*loc. cit.*).

TABLE IV.

Results (vide Fig. 4: acid melting at 0.9° \equiv 88.3% acid).

% Gasoline.	C.S.T.	% <i>cyclo</i> - Hexane.	C.S.T.	% Toluene.	C.S.T.
1.47	16.7°	2.89	18.45°	0	14.9°
2.86	19.0	4.48	20.6	24.77	20.95
8.4	27.1	13.72	32.9	44.57	26.3
14.47	36.1	14.2	33.3	75.25	34.5
18.35	43.3	0	14.9	81.04	36.35
0	14.9			94.14	40.35
				100.00	41.8
% Thiophen.	C.S.T.	% <i>n</i> -Butyl alcohol.	C.S.T.		
0	14.9°	0	14.9°	Acetic acid	
31.3	10.6	1.21	9.9	used had	
75.3	5.1	3.78	6.2	m. p. 0.9	
100	1.9	5.81	7.8	\equiv 88.3% acid.	
Acetic acid		8.65	14.2		
used had		11.07	3.8		
m. p. -2.2°		1% <i>n</i> -Butyl alcohol lowers c.s.t. by 1.3°.			
\equiv 85.7% acid.		44.5	29.8		
Acetic acid		49.4	4.3		
approx. 39%.		1% <i>n</i> -Butyl alcohol lowers c.s.t. by 1.2°.			
Acetic acid		68.1	16.9		
approx. 50%.		71.23	4.8		
		1% <i>n</i> -Butyl alcohol lowers c.s.t. by 5.9°.			

The low-boiling petroleum fraction and *cyclohexane* produce very similar effects, the former raising the critical solution temperature values slightly more than the latter.

1 per cent. of *cyclohexane* raises the critical solution temperature by 1.25°
 1 per cent. of petroleum " " " " " " " 1.46°.

The critical solution temperature method was used to estimate the concentration of *n*-butyl alcohol in benzene for experiments on adsorption from solution, first with low concentrations of the alcohol, but afterwards throughout the whole range up to 100 per cent. alcohol. This forms a very interesting example of the value of the method. As will be seen from Fig. 4 and Table IV, the alcohol has such a large effect that, with one concentration of acid, one gets rapidly below ordinary temperature ranges. It was necessary, therefore, as the concentration of the alcohol increased, to dilute the acid used. The results given below show that up to more than 70 per cent. *n*-butyl alcohol, when the acetic acid had been diluted to 50 per cent., a change of 1 per cent. in the alcohol concentration still gave almost the same change in the critical solution temperature (3.9° instead of 4.3°) as when the concentration of alcohol in the benzene was only 1 per cent. and the acid concentration more than 90 per cent. This provided, therefore, an extremely accurate and rapid method of estimating *n*-butyl alcohol in benzene throughout the entire range of concentrations. The critical phenomena were, moreover, very clear and distinct.

For higher concentrations of *n*-butyl alcohol, the ternary critical solution temperature obtained with 14 per cent. hydrochloric acid and *n*-butyl alcohol, which is so extraordinarily sensitive to impurities of the nature of benzene, was used (1 per cent. of toluene was found to raise the upper and depress the lower ternary critical solution temperature of *n*-butyl alcohol-hydrochloric acid by 19°; *loc. cit.*).

Carbon Disulphide-Aqueous Acetic Acid. Estimation of Sulphur in Carbon Disulphide.—The carbon disulphide was a purified material (Merck) which gave negative tests to ordinary impurities, and on one distillation through a 12-bulb pear still-head, gave the following results :

	Volume(c.c.).	C.S.T.
1st fraction	50	12.2°
2nd "	50	12.4
3rd "	100	12.4
4th "	50	50
Residue	30	12.2

The third fraction was taken as sufficiently pure.

The critical solution temperature taken with acetic acid melting at 15.3° proved very sensitive to the presence of sulphur, as shown in Fig. 5 and Table V, linear relations being found. One per cent. of sulphur raises the critical solution temperature by 4.7°, so that it could be estimated accurately by this method to 0.02 per cent.

One per cent. of benzene produces a lowering of 1.5°. *cyclo*Hexane gave a critical solution temperature of 15.0° with the same acetic acid. Lower petroleum (b. p. 65–69°) gave a critical solution temperature of 8.45°.

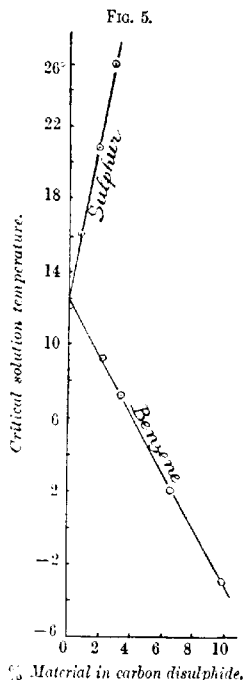


TABLE V.

Results (*vide* Fig. 5).

% Sulphur.	C.S.T.	% Benzene.	C.S.T.
0	12.4°	0	12.4°
0.77	15.95	2.2	9.2
1.9	20.7	3.4	7.2
2.8	25.4	6.5	1.9
		9.75	-3.0

Important Practical Conclusions.

The experimental work done on these binary and ternary critical solution temperatures, from the point of view of their use as criteria of liquid purity, may be summed up in the following conclusions:

(A).—In the case of both binary and ternary critical solution temperatures, each impurity has its specific effect which must be determined before one can judge of the value of the method for indicating its presence, for example, homologues may or may not have a large effect. Thus the effect of the lower and the higher acid homologues on the critical solution temperature of *n*-butyric acid-water would be very large, whilst that of petroleum homologues on the acetic acid-petroleum system is very small, owing to the large difference in the solubility relations among the fatty acids. Further, although the effect of any material, considered as impurity, may usually be foretold to some extent from its general solubility relations and from the usual effects produced by certain groups, sometimes this is not the case; for example, the effect of dinitrobenzene on the critical solution temperature of nitrobenzene. Especially does this occur when the critical line shows marked deviation from the linear, for example, toluene-aniline, toluene-methylaniline. (Results as yet unpublished.)

(B).—The presence as impurity of the second component will not be indicated at all by observation of a binary critical solution temperature. This becomes of great importance in cases where the second component is the common impurity, for example, water in phenol, *n*-butyric acid, or *n*-butyl alcohol. A ternary critical solution temperature does not suffer from this defect, although of course the effect may be small.

(C).—A critical solution temperature method is admirably adapted by its simplicity and accuracy for following a course of purification, say, by distillation, chemical treatment, or fractional freezing. It must be emphasised that if, for instance, distillation is the process of purification adopted, complete homogeneity of material, as far as can be obtained by the purification method, and as tested by the critical temperature method, can only be assumed when relatively small initial and final fractions give the same value as the main fractions.

(D).—It is always necessary to guard against the possible mutual effects of different impurities. Thus, in distilling impure *n*-butyl alcohol, in a first fraction one would get water and the lower homologues, impurities of practically the same volatility, and yet having quite opposite effects on the critical solution temperature of the

ternary mixture with hydrochloric acid, the homologues lowering, and the water raising, the critical solution temperature. Further treatment, however, usually reveals the non-homogeneity of the fraction.

(E).—The so-called binary critical solution temperatures are employed until the liquid to be tested is finally purified, but the system is not binary and therefore it may be very necessary to use definite proportions. Hence the use of the accurate pipettes for the precise adjustment of concentration required in determining ternary critical solution temperatures is recommended also in the case of binary critical solution temperatures.

My best thanks are due to the staff of Johns Hopkins University for giving me every facility for carrying on the research, to Prof. K. J. P. Orton for originally suggesting it, and to Prof. F. G. Donnan. During this research, I was part-time an 1851 Exhibitioner of Wales and later a National Research Fellow of U.S.A.

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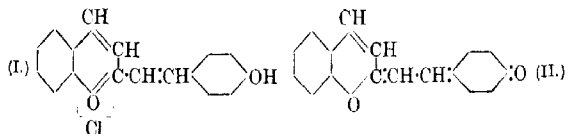
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[Received, November 2nd 1922.]

CLXII.—*Benzopyrylium Salts of Distyryl Ketones.* *Part II. Salts and Metallic Complexes of* *4'-Dimethylamino-2-styrylbenzopyrylium.*

By JOHANNES SYBRANDT BUCK and ISIDOR MORRIS HEILBRON.

In a former communication (T., 1922, **121**, 1198), it has been shown that whereas 4'-methoxy-2-styrylbenzopyrylium chloride dissolves in water giving a red solution which does not alter in colour on dilution, the solution of the corresponding 4'-hydroxy-2-styrylbenzopyrylium chloride (I) changes from deep red to pure blue on high dilution. This alteration in colour was attributed to an intermolecular rearrangement from the benzenoid pyrylium to the quinonoid pyrone (II), a rearrangement obviously impossible in the case of the 4'-methoxy-salt.



With a view to study further the interesting colour changes of these styrylpyrylium salts, and with the hope of obtaining new

evidence in support of the above suggestions, a series of salts derived from 4'-dimethylamino-2-hydroxydistyryl ketone has now been prepared, these being, so far as we are aware, the first of their class in which a typical basic group is associated with the pyrylium nucleus.

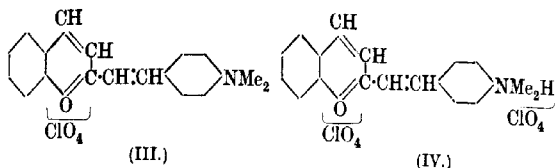
Owing to the presence of the dimethylamino-radicle in the molecule, a difficulty in the mode of preparation is introduced, as this group renders the pyrylium salts exceedingly soluble in the usual acid media employed for their preparation, and as a result of this we have been unable to isolate the free chloride in the solid state.* Its formation, as also the alteration in structure which it undergoes, can conclusively be inferred from the remarkable colour changes which take place, as indicated in the following table, on heating the ketone with concentrated hydrochloric acid, followed by subsequent dilution of the solution with water.

From 0.25 gram of ketone.

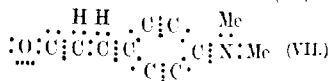
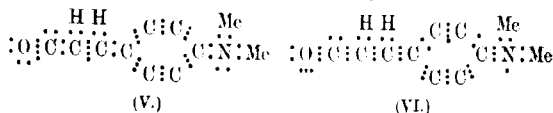
Colour.	Volume of solution in c.c.
Blood-red (cold solution)	10
Golden-yellow (after heating)	10
Pale green	12
Intense emerald-green	18
" dark crimson	30
" red-violet	150
Pure violet	300
Blue with violet tint	800-1800
Deep blue	2500
Intense royal blue	3500
Distinct blue solution	10*

Attempts were also made to prepare the pyrylium iodide, but although here brown or green products were actually obtained in crystalline form, these proved on analysis to be complicated periodides to which we have been unable to assign any definite formulae. On the other hand, two distinct *perchlorates* have been isolated. The first of these, which forms olive-green crystals, is similar in appearance to the colour-base, obtained by the addition of dilute potassium carbonate solution to a solution of the chloride, and thus would correspond in structure to formula (III). The second salt, which is orange-yellow, contains an extra molecule of perchloric acid and doubtless corresponds to a simple perchlorate of the pyrylium salt (Formula IV).

* Although it has been found impossible to obtain the solid pyrylium chloride in the case now under consideration, we have succeeded in doing this both with the closely related 7-hydroxy-2-styryl-4-methylbenzopyrylium and the corresponding phenyl homologue. The preparation and description of these salts will form the subject of a further communication.

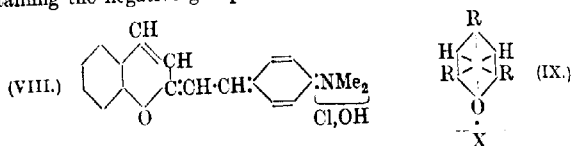


As regards the colour changes observed on treatment of the ketone itself with hydrochloric acid, we suggest that the primary red colour is the typical halochromic phenomenon observed generally among the distyryl ketones (Bayer and Villiger, *Ber.*, 1902, **35**, 1189) and that ring-closure is only brought about on heating, the golden-yellow solution thus containing the hydrochloride analogous in structure to (IV). On dilution with water, hydrolysis of this salt would result, the green acid solution now containing mainly undissociated pyrylium chloride in which the enhanced colour can be attributed to the presence of the free NMe_2 -group, which is again able to exert its full auxochromic influence. With continued dilution, increasing ionisation of the salt must occur, with the result that the electrostatic forces holding the anion to the positively charged oxygen atom will certainly become weakened and the subsequent colour phenomena may readily be accounted for by structural alterations in which the kation alone is involved. Such a suggestion is in strict agreement with the electronic conception of valency, the changes solely involving a regrouping of the electrons within the octets (compare Kermack and Robinson, *T.*, 1922, **121**, 427). On this basis, the limiting phases would correspond to (V) and (VII), in which the latter coincides with the usual quinonoid form. In this the anion is regarded as being bound by electrovalence forces



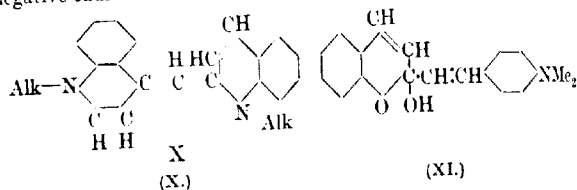
to the ammonium radicle (VIII), this condition corresponding to the blue solution, and being quite analogous to the case of 4-hydroxy-2-styrylbenzopyrylium chloride. Between these two extreme conditions, a further kationic phase is readily conceivable (formula VI) and the red solution formed on further dilution of the green solution with water could thus be accounted for. In this condition of the molecule, we consider the negative ion as being held, not to

any specific atom, but co-ordinated with the kationic complex as a whole. It is noteworthy that the red phase is entirely suppressed when alcohol or acetone is employed as solvent. A somewhat similar conclusion to this has been drawn by Diltney in his study of the quinopyran derivatives (*Ber.*, 1920, **53**, [B], 261), the pyrylium salts in this series being represented (formula IX) as simply containing the negative group in a second zone, and not attached to



any particular individual atom.

Further, König and Treichel (*J. pr. Chem.*, 1921, [iii], **102**, 63) have obviously the same conception in mind in the partial valency formula (X) employed by them to represent the attachment of the negative radicle in the case of the isocyanine dyes.*



Attempts were made to isolate quinonoid salts in the solid state, and it was hoped that a blue perchlorate might be obtained. The addition of excess of perchloric acid to the blue solution of the chloride precipitates, however, the ordinary green perchlorate, the action here being the reverse to that of water, but the red and violet stages are entirely suppressed. On the other hand, ferrocyanic acid gives a brilliant blue precipitate which is probably a quinonoid salt of type VIII. Further support to our views regarding the existence of a quinonoid form is evidenced by the transformations which the colourless carbinol base (XI) undergoes. This substance, which has been isolated in an impure state by treating the pyrylium perchlorate with aqueous potassium hydroxide, is readily soluble in alcohol, giving a solution which, on being poured into a large

* It is interesting to note that, in the current number of *Chemistry and Industry* (p. 414), Professor Lowry has ingeniously elaborated, from purely theoretical deductions, a polar formula for the thiocyanines which is absolutely analogous to that now suggested by us, and which harmonises with König and Treichel's partial valency conception (*loc. cit.*). The present communication was completed before Professor Lowry's article had appeared.

volume of water, forms a colourless suspension. This in turn rapidly dissolves, yielding the same deep blue solution as is obtained from the chloride. From analogy with the 4'-hydroxy-salt there can be little doubt that this contains the quinonoid ammonium base.

Metallic Complex Salts.—Although the chloride has not itself been obtained, we have been able to isolate a remarkable series of crystalline metallic complexes, the preparation of which is described in the experimental part. These are doubtless analogous to the so-called metallic double salts obtained by Fosse and Lesage (*Compt. rend.*, 1905, **140**, 1402; **141**, 625; 1906, **142**, 1543) in the dinaphthapyrylium and xanthylum series. With bivalent metals such as copper, cobalt, cadmium, and zinc, the complexes have the general formula $C_{19}H_{18}ONCl, HCl, MCl_2$. The *ferripyrylium chloride*, on the other hand, differs in having no acid addendum, but this is exceptional, as both the *thallipyrylium chloride* and the *stannipyrylium chloride* crystallise with such. We suggest that these salts, which are all very similar in appearance, being well-defined, crystalline substances, yellow or green in colour, are typical pyrylium complexes, identical with the perchlorate in structure. They are all very readily soluble in water, giving, on just moistening, green, crystalline solids which are converted on further addition of water, first into a pure violet, and then into the characteristic blue substance to which we have attributed the quinonoid pyrone structure. In the case of the metallic complexes also, dilution with alcohol or acetone entirely suppresses the violet phase.

EXPERIMENTAL.

4'-Dimethylamino-2-styrylbenzopyrylium Perchlorate.—Three grams of 4'-dimethylamino-2-hydroxydistyryl ketone (chloroform additive product), prepared according to the method of Heilbron and Buck (T., 1921, **119**, 1500), were dissolved in 20 c.c. of concentrated hydrochloric acid, and the red solution was heated until the characteristic change in colour was effected. The solution was then diluted to about 2 litres with water (deep purple colour) and treated with 5 c.c. of 20 per cent. perchloric acid. The dark green, flocculent precipitate was filtered, dried, and recrystallised from glacial acetic acid, after which it was left to stand for some months in an exsiccator over sodium hydroxide, this treatment being necessary in order to free it entirely from acid addenda. The salt is obtained in dark green, glittering prisms, "puffing" when heated, and melting at 207°. It is only very sparingly soluble in water, alcohol, or acetone, giving a deep royal blue solution (Found: C = 60.6; H = 5.1. $C_{19}H_{18}ON \cdot ClO_4$ requires C = 60.7; H = 4.8 per cent.).

The *diperchlorate*, $C_{19}H_{18}ON \cdot ClO_4 \cdot HClO_4$, was obtained by heating the ketone (5 grams) with 20 c.c. of concentrated hydrochloric acid until the pyrylium salt solution was produced. After cooling, and without further dilution, 70 per cent. perchloric acid was cautiously added and the yellow precipitate filtered off and recrystallised from concentrated hydrochloric acid. The salt forms pale orange-coloured needles exceedingly unstable when moist, moderately stable when dry. Treatment with water, alcohol, etc., produces the normal perchlorate. It explodes with extreme violence on heating, so that for analysis it is necessary to mix the compound with a large excess of powdered quartz, close the upper end of the combustion tube, and then very gradually decompose the salt by heating, after which the tube is burnt out as usual (Found: C = 47.1; H = 4.2. $C_{19}H_{18}ON \cdot ClO_4 \cdot HClO_4$ requires C = 46.9; H = 3.9 per cent.).

4'-Dimethylamino-2-styrylbenzopyrylium Ferrocyanide.—This salt was prepared by the addition of potassium ferrocyanide solution to the dilute, blue, acid solution of the pyrylium chloride. It was precipitated as a brilliant blue powder, practically insoluble in cold water, somewhat soluble in hot glacial acetic acid with a deep blue colour, and very sparingly soluble in all other solvents. As with all other compounds of this series, the ferrocyanide dissolves in cold concentrated sulphuric acid with a yellow colour, but it is unique in that the solution shows a marked greenish-yellow fluorescence [Found: C = 60.8; H = 4.4; Fe = 11.3. $C_{19}H_{18}(ON, H_3Fe(CN)_6$ requires C = 61.1; H = 4.3; Fe = 11.4 per cent.).

Picric acid.—A bulky green precipitate is obtained by treating a dilute (purple) solution of the pyrylium chloride with alcoholic picric acid. On drying and recrystallising the product, a mixture of bright green and almost black crystals is obtained. These could not be separated, being apparently interconvertible.

Bases of 4'-Dimethylamino-2-styrylbenzopyrylium Chloride.—As in the case of other salts of this type (Buck and Heilbron, *loc. cit.*), these could not be obtained crystalline, or sufficiently pure for trustworthy analysis. The *colour base* is precipitated by the addition of excess of potassium carbonate solution to a violet solution of the chloride. Potassium acetate, the usual reagent, gives no precipitate, the violet solution persisting. The colour base forms dull green flocks, which, after long drying on a porous plate, yield a sage-green powder insoluble in water, but soluble in alcohol or acetone to a deep yellow-green solution, from which it is reprecipitated on dilution. The alcoholic solution gives a deep emerald colour with dilute acetic acid, and a greenish-blue colour with hydrochloric acid, both colours persisting on dilution. When warmed with hydro-

chloric acid, the alcoholic solution gives a deep green colour; with excess of acid this becomes orange-red, and gives a fine blue colour on dilution.

The *carbinol* base is obtained by suspending about 1.0 gram of the pure perchlorate in 20 c.c. of absolute alcohol, and then adding 2 c.c. of 25 per cent. potassium hydroxide solution. The salt slowly dissolves, yielding a pale yellow solution from which, by the addition of water, a colourless gel separates. On standing over-night, this settles out as a very pale yellow, flocculent precipitate which cannot, however, be entirely freed from potassium, for repeated washing with water causes resinification of the product. The impure base when dry forms a pale yellow powder which is somewhat sparingly soluble in alcohol or acetone, giving a light yellow solution. It is soluble in glacial acetic acid with an intense royal blue colour. In cold concentrated hydrochloric acid, the base dissolves to an orange-yellow solution which becomes blue on high dilution. If an alcoholic solution be poured into a large volume of water, a white emulsion is first formed which rapidly redissolves with formation of the characteristic blue solution. The same change is produced by largely diluting an alcoholic solution with alcohol, but does not take place when acetone is used as diluent. The change is undoubtedly due to the conversion of the carbinol base (XI) into the quinonoid colour-base (VIII). As in the case of the blue solution produced directly from the chloride, ether extracts no blue colouring matter, but gives only a faintly yellow layer.

Metallic Complexes of 4'-Dimethylamino-2-styrylbenzopyrylium Chloride.

The general method of preparation of these compounds is as follows: 5 grams of the ketone are dissolved in 30 c.c. of concentrated hydrochloric (or hydrobromic) acid, and the red solution is heated until pyrylium salt formation is brought about. While still warm, the solution is treated with an equal weight of the metallic chloride (or bromide) dissolved in from 10 to 15 c.c. of water. On gently warming the mixture, the whole rapidly sets to a crystalline mass. The product is filtered off and repeatedly washed with small quantities of concentrated acid and dried, first in an exsiccator over sodium hydroxide, and then in a vacuum at 100° for several hours. The salts can in most cases be recrystallised from concentrated hydrochloric acid, but the process is wasteful and unnecessary, as they crystallise out from the original solution in a state of purity. Although stable in the dry state, they decompose fairly rapidly on exposure to moisture, yielding pure green solids with a lower chlorine content. The metallic complexes are all very readily

soluble in water, giving in the first place deep violet solutions which quickly change to blue on dilution. On treatment of the latter with hydrochloric acid, the reverse colour change occurs and, on carefully increasing the amount of free acid, green and then yellow solutions obtain. All the salts are somewhat soluble in alcohol, acetone, or glacial acetic acid, giving blue solutions. It is interesting to note that strontium chloride and aluminium chloride could not be induced to form complexes, whilst the *chloroaurate*, which separates out in a green form and is apparently of the same type as the ferrichloride, is too unstable to isolate in a pure state. The complexes, although very similar, vary slightly; thus the violet stage persists longer with the *zinc chloride* salt than with the *ferrichloride* salt, and the *cuprichloride* salt is more soluble than the *cobalt chloride* salt. With ammonium hydroxide, the alcoholic solutions give generally a dirty violet colour and a precipitate of the metallic hydroxide.

Cupri-salt, $C_{19}H_{18}ONCl.HCl.CuCl_2$.—This salt is obtained in the form of ochre-coloured, microscopic needles, melting with decomposition at $171-172^\circ$. That the metal is present as a complex ion is readily shown by the fact that a solution of the salt fails to deposit any cupric sulphide whatsoever on saturation with hydrogen sulphide. The addition of acid in sufficient quantity to form the yellow solution yields a similar negative result [Found: C = 47.7; H = 4.1; Cl (Carius) = 29.5. Calc., C = 47.3; H = 4.0; Cl = 29.4 per cent.].

Cobalt Salt, $C_{19}H_{18}ONCl.HCl.CoCl_2$.—This forms brilliant apple-green, prismatic crystals melting at $214-215^\circ$ (Found: C = 47.6; H = 4.0; Cl = 29.6. Calc., C = 47.7; H = 4.0; Cl = 29.7 per cent.).

The *cadmium* salt crystallises out in greenish-yellow needles melting at $218-220^\circ$ (Found: C = 43.0; H = 3.7; Cl = 27.2. $C_{19}H_{18}ONCl.HCl.CdCl_2$ requires C = 42.9; H = 3.6; Cl = 26.7 per cent.), whilst the analogously constituted *zinc* salt is obtained in golden, glistening needles which melt at 218° (Found: C = 47.0; H = 4.1; Cl = 28.9. $C_{19}H_{18}ONCl.HCl.ZnCl_2$ requires C = 47.2; H = 4.0; Cl = 29.3 per cent.).

Cadmium Bromide Salt.—Five grams of the benzene additive product of the ketone are dissolved in 30 c.c. of hydrobromic acid solution (*d* 1.7), and the solution heated in order to form the pyrygium bromide, which is then treated with 5 grams of cadmium bromide dissolved in 10 c.c. of dilute hydrobromic acid. A crystalline mass separates out almost immediately and this is filtered off, thoroughly washed with concentrated hydrobromic acid, and dried in the usual manner. The complex salt is obtained in ochre-coloured, glistening

crystals which change to orange at 120° and melt at $214\text{--}215^{\circ}$ (Found: C = 31.9; H = 2.8. $\text{C}_{19}\text{H}_{18}\text{ONBr}, \text{HBr}, \text{CdBr}_2$ requires C = 32.3; H = 2.7 per cent.).

The *ferri*-salt is prepared by dissolving 4 grams of either the chloroform or benzene additive product of the ketone in 50 c.c. of hot absolute alcohol, and treating the solution with 10 grams of commercial ferric chloride dissolved in 30 c.c. of warm concentrated hydrochloric acid. An intensely green solution is produced which rapidly becomes pasty. More acid is added and after heating on a water-bath for a few minutes the product is filtered off, washed with concentrated hydrochloric acid, and dried in an exsiccator. The crude salt is finally purified by recrystallisation from a mixture of acetone and benzene. It adheres very tenaciously to benzene, the last traces of which are removed only by heating in a steam-oven. The salt forms bronze-green, glistening, prismatic needles which melt with decomposition at 227° . Unlike the other metallic complexes, it is obtained anhydrous, although, as various analytical results have indicated, it undoubtedly tends to form an additive product with benzene (Found: C = 48.0; H = 4.0; Fe = 11.7. $\text{C}_{19}\text{H}_{18}\text{ONCl}, \text{FeCl}_3$ requires C = 48.1; H = 3.8; Fe = 11.8 per cent.).

Stanni-salt, $\text{C}_{19}\text{H}_{18}\text{ONCl}, \text{HCl}, \text{SnCl}_4, \text{H}_2\text{O}$.—This salt is prepared by the addition of stannic chloride drop by drop to the green pyrylium chloride solution. The yellowish-green precipitate is filtered off, dried, and the ochre-coloured powder which results is redissolved in a small quantity of water, filtered, and treated with an excess of concentrated hydrochloric acid. On standing, long, slender prisms separate out, having a characteristic greenish-yellow colour. The salt melts at 224° , a distinct change being evident at 170° , when the crystals change to a pale green powder, this doubtless being due to loss of water (Found: C = 36.4; H = 3.6; Cl = 34.0. Calc., C = 36.3; H = 3.3; Cl = 34.0 per cent.).

Thalli-salt, $\text{C}_{19}\text{H}_{18}\text{ONCl}, \text{HCl}, \text{TiCl}_3$.—Five grams of thalious chloride, suspended in 20 c.c. of water, are treated with chlorine until a clear solution results, when 40 c.c. of concentrated hydrochloric acid are added. The whole is then cautiously added to the pyrylium chloride solution obtained from 5 grams of the ketone, dissolved in 40 c.c. of concentrated hydrochloric acid. Some gummy matter separates out at first and is removed from the solution by filtration, the pure salt being then deposited as a greenish-black, microcrystalline mass. The compound is peculiar in being only slightly soluble in water, but it is readily soluble in acetone, giving an intense blue solution, from which benzene precipitates a mass of tiny, green needles. The blue acetone solution gives with dilute

hydrochloric acid a violet precipitate which changes to green on the addition of further acid, while with a large excess of acid a yellow solution is formed (Found: C = 34.5; H = 3.2. $C_{19}H_{18}ONCl, HCl, TiCl_3$ requires C = 34.6; H = 2.9 per cent.).

In conclusion, one of us (J. S. B.) wishes to express his gratitude to the Royal Commissioners for the Exhibition of 1851 for a grant which has enabled this work to be carried out.

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[Received, May 1st, 1923.]

CLXIII.—*Optical Rotations of the Sugars. Part II, The Methyl Pentoses and the Glucosides.*

By JOHN GWILLIAM MALTBY.

THE method previously described for investigating the rotations of the sugars (T., 1922, 121, 2608) has been extended to the methyl pentoses and the glucosides.

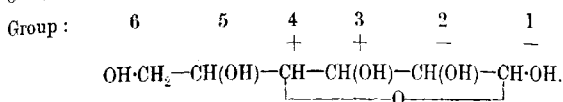
So far it has been shown that van't Hoff's theory of optical superposition applies to the aldoses and their derivatives. The rotation due to the asymmetric groups other than group 1 is the mean of the rotations of the α - and β -forms, and is called the $(\alpha + \beta)/2$ value; the difference between these values for epimeric sugars is constant, and its sign divides the sugars into two groups. The distinction between the α - and β -forms has been shown to depend on the relative configurations of groups 1 and 3, and the mechanism of the cyanohydrin synthesis also depends on the latter. Rules have been formulated by which it is possible to determine from the rotation whether a sugar is the α - or the β -form.

The molecular rotational values found for the asymmetric groups are given in Table I.

TABLE I.

Group	5	4	3	2	1	
Pentoses		60			84	Sugars
Methyl pentoses		60	60	60	184	Methyl glucosides
Hexoses	30	30			324	Phenyl glucosides

These figures have been obtained from experimental values which have been "rounded off" in order to simplify the graphs and calculations. They show that a change in constitution at one end of the molecule has no large effect on the other end. The negative sign ascribed to group 1 follows from the configuration given to α -glucose by Böseken (*Ber.*, 1913, 46, 2612), Michaelis (*ibid.*, 3683), and Pictet (*Helv. Chim. Acta*, 1920, 3, 649). Thus



It thus seems that the abnormalities of xylose (Carruthers and First, T., 1922, **121**, 2299) are not due to the presence of an amylene-oxidic structure, as stated by Irvine (this vol., p. 918).

The Methyl Pentoses.—Proceeding as for the pentoses and hexoses, Fig. 1 is obtained for the rotations of the α , equilibrium, and β -forms of those methyl pentoses with a positive $(\alpha + \beta)/2$ value (*loc. cit.*).

Sugar.	Configuration.	5	4	3	2
Rhodose	1	+	1	-
IsoRhannose	-	-	+	+
Epirhodose	+	+	+	+
Rhannose	+	+	-	-

$\alpha \div \beta$
 equilibrium.

Rhamnose, in which group 3 is negative, is abnormal with regard to its α - and β -rotations (Hudson and Yanovsky, *J. Amer. Chem. Soc.*, 1917, **39**, 1013), and isorhamnose, in which group 4 is negative, is abnormal also, since it does not form a hydrazone with diphenylmethanedimethyldihydrazine (Votoček, *Z. Zuckerind. Böhm.*, 1919, **43**, 574). On solving the equations derived from the rotations and configurations, the two sets of values given in Table II are obtained for the rotational value of each group according to the configuration given to group 5 in rhodose.

TABLE II.

Group	5	4	3	2	1	
(1)	?	+40°	?	-60°	-84°	Also group 5-group 3 = -60°.
(2)	?	?	+60°	-60°	-84°	Also group 5-group 4 = +40°.

The second set seems the more probable, in which groups 1, 2, and 3 have the same values as the corresponding groups in the pentoses and hexoses. This means that rhodose has the configuration

5	4	3	2
+	+	+	-

and not that suggested by Mayer and Tollens (*Ber.*, 1907, 40, 2434).

The Glucosides.—Since the $(\alpha + \beta)/2$ values of the pentoses, hexoses, and methyl pentoses are now known, the rotations of their methylglucosides can be calculated, since the difference between the molecular rotations of the α - and β -methylglucosides of various sugars is constant, and their mean is the same as that of the α - and β -sugars from which they are derived (Hudson, *J. Amer. Chem. Soc.*, 1909, 31, 66).

With the methylglucosides, group 1 has a rotational value -184° , and with the sugars it is -84° , so that the molecular rotations of the former differ by 100° from those of the latter.

Table III gives the calculated rotations of the methylglucosides derived from the pentoses, hexoses, and methyl pentoses, with positive $(\alpha + \beta)/2$ values. In those cases where the rotations are known (the values are given in brackets) the calculated rotations agree fairly well with the experimental values. A large discrepancy occurs only in the case of β -methylarabinoside, small discrepancies being shown by the methylmannoside and the methylrhamnosides, these being derived from the sugars with abnormal rotations for their α - and β -forms (Hudson, *loc. cit.*).

TABLE III.

Methyl	α .	β .	Methyl	α .	β .
arabinoside	$+364^\circ$ ($+403^\circ$)	-4° ($+120^\circ$)	galactoside	$+364^\circ$ ($+347^\circ$)	-4° (0°)
riboside	$+244^\circ$	-124°	glucoside	$+304^\circ$ ($+305^\circ$)	-64° (-64°)
xyloside	$+244^\circ$ ($+249^\circ$)	-124° (-108°)	altroside	$+304^\circ$	-64°
lyxoside	-124°	$+244^\circ$	taloside	$+244^\circ$	-124°
			idose	$+244^\circ$	-124°
			gulose	$+244^\circ$	-124°
			mannoside	-184° (-160°)	$+184^\circ$ ($+184^\circ$)
			alloside	-184°	$+184^\circ$

Methyl	α .	β .
rhodose	$+344^\circ$	-24°
isorhamnoside	$+264^\circ$	-104° (-100°)
epirhodose	$+224^\circ$	-144°
rhamnoside	-144° (-121°)	$+224^\circ$ ($+170^\circ$)

PART II. THE METHYL PENTOSEs AND THE GLUCOSIDES. 1407

It has been shown that the rotational value of group 1 increases fairly regularly with the molecular weight of the alcohol group in the aliphatic series (Bourquelot, *Bull. Soc. chim.*, 1913, [iv], **13**, xiii; Hudson, *J. Amer. Chem. Soc.*, 1909, **31**, 66).

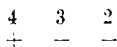
Knowing the $(\alpha + \beta)/2$ values for the sugars, we can calculate the approximate rotational values of group 1 for the glucosides of the various alcohols (Table IV).

TABLE IV.

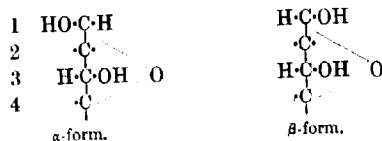
Sugars.	Methyl.	Ethyl.	Propyl.	Butyl.	Amyl.	Allyl.	Benzyl.	Phenyl.
	-84°	-184°	-194°	-200°	-210°	-216°	-210°	-270° -324°

These values hold for the glucosides of the various sugars, the only exception being α -benzylarabinoside, which has a calculated value of $[M]_D = 450^\circ$. The experimental value is higher than this ($[M]_D = 516^\circ$; Fischer and Beensch, *Ber.*, 1894, **27**, 2482), but the authors themselves state that there may be a large error, since a very dilute solution was used.

The Isomerism of the α - and β -Forms.—The sign of the $(\alpha + \beta)/2$ value has been shown to divide the sugars into two groups, since for those with a positive $(\alpha + \beta)/2$ value the ratio of the isomeride with the higher positive rotation to the other isomeride in the equilibrium mixture is 1 : 2. In the previous paper (*loc. cit.*), the former was taken to be the α -form, the latter the β -form. It has now been found that for mannose and rhamnose this is the converse of the distinction given by the action of enzymes, the mode of preparation, and the rate of hydrolysis of the glucosides. Again, in the case of the α - and β -tetramethyl methylmannosides (Irvine and Moody, *T.*, 1905, **87**, 1462), the physical properties are the converse of those of other corresponding compounds. Now these two sugars both have the configuration



and sugars with this configuration have been shown to be abnormal as regards the rotations of their α - and β -forms (Hudson and Yanovsky, *J. Amer. Chem. Soc.*, 1917, **39**, 1013). These sugars, which comprise lyxose, mannose, gulose, and rhamnose, are the only sugars with a positive $(\alpha + \beta)/2$ value and yet with group 3 negative. Since group 1 has a negative rotational value, the configurations of the α - and β -forms can be determined from their rotations, and it is found that for the α -form groups 1 and 3 have opposite configurations, whilst for the β -form they have the same configuration.



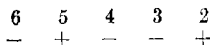
Thus the α -form has a greater numerical rotation than the β -form, except in the case of lyxose, mannose, gulose, and rhamnose, where the converse holds good. This difference enables the α -form to be distinguished from the β -form by their rotations, where these are known accurately. This method of distinction can be applied to most derivatives of the sugars, but the sugars themselves show mutarotation, so that the rotations cannot always be easily found. But the sign of the $(\alpha - \beta) \cdot 2$ value is the same as that of the equilibrium mixture, except in the case of sugars with an $(\alpha + \beta) \cdot 2$ value less than one-sixth of the difference between the rotations of the α - and β -forms, namely, mannose and allose. Thus if the rotation diminishes to the equilibrium value, the isomeride originally present was the α -form, whereas if it increases, or if it changes sign, the isomeride was the β -form, except in the case of lyxose, gulose, allose, and rhamnose, where the converse holds good. The above two rules are easier to apply than that of Hudson (*J. Amer. Chem. Soc.*, 1909, **31**, 66).

Knowing the configurations of the α - and β -forms of the sugar, it has now been found that the isomeride formed in larger quantity by the cyanohydrin synthesis always has the same configuration as the α -form of the sugar, since the configuration of group 2 in the product is always the opposite of that of group 4. This is shown in Table V.

TABLE V.

Sugar.	Config- uration.	Main product.	Config- uration.	Reference.
	5 4 3 2		6 5 4 3 2	
Arabinose		Mannonitrile		Fischer, <i>Ber.</i> , 1890, 23, 2613.
Xylose		Gulonitrile		Fischer and Fay, <i>Ber.</i> , 1895, 28 , 1975.
Ribose		Altronitrile		Leveno and Jacobs, <i>Ber.</i> , 1910, 43 , 3141.
Glucose		α -Glucoheptono- nitrile		Fischer, <i>Annalen</i> , 1892, 270 , 72.
Mannose		α -Mannohepto- nitrile		Peirce, <i>J. Biol. Chem.</i> , 1915, 23 , 327.
Galactose		α -Galaheptono- nitrile		Peirce, <i>ibid.</i>
*Rhamnose		α -Rhamnohexo- nitrile		Fischer and Morrell, <i>Ber.</i> , 1894, 27 , 390.

Therefore α -guloheptononitrile (La Forge, *J. Biol. Chem.*, 1920, **41**, 251) will have the following configuration



In conclusion, the author wishes to thank Prof. F. S. Kipping, F.R.S., for his interest in this work.

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[Received, March 17th, 1923.]

(CLXIV.—*Estimation of Tin in Wolfram. A Modification of Powell's Method.*

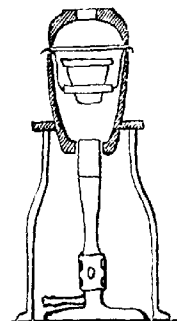
By OCTAVIUS FRANCIS LUBATTI.

THE method described below for the estimation of tin in wolfram, which differs from Powell's method (*J. Soc. Chem. Ind.*, 1918, **37**, 285r) in that zinc vapour (Beringer, "Text-book of Assaying," p. 285) is used instead of sodium peroxide for the decomposition of the tin residue, offers the following advantages: (a) sodium peroxide, which does not keep well in a hot, damp climate, is not used, (b) by the use of zinc and zinc oxide, the cost of the reagents is about halved, and (c) fusion in an iron crucible is avoided.

Principle of the Method.—Wolfram ores, when fused with potassium pyrosulphate, are decomposed with the formation of potassium tungstate. The product of the fusion is treated with a solution of tartaric acid, which dissolves tungsten salts but not silica and tin compounds. The residue is collected on a filter, ignited, mixed with the zinc reducing mixture and decomposed in a suitable furnace. The tin, obtained in the metallic state together with zinc and zinc oxide, is dissolved in hydrochloric acid saturated with chlorine, and the solution, after reduction with metallic antimony, is titrated with a standard solution of iodine in the usual manner.

The Furnace.—Any small crucible furnace capable of withstanding a temperature of about 1000° is suitable for the purpose. The author uses an ordinary Battersea No. 3 fireclay crucible with a hole in the bottom 4 cm. in diameter (Fig. 1) and covered at the top with a No. 4 scorifier, which is also provided with a hole

FIG. 1.



in the bottom 5 cm. in diameter. The reduction takes place in a small porcelain crucible of 15 c.c. capacity, supported in the central part of the furnace by means of a silica triangle, attached with nickel hooks to the sides of the crucible. The heat is supplied by a No. 4 Mecker burner.

Standard Iodine Solution.—An approximately $N/100$ -iodine solution is standardised against a tin solution prepared as follows: 0.2 gram of pure tin is dissolved in 50 c.c. of concentrated hydrochloric acid by heating gently, the solution is cooled and made up to 500 c.c., and 50 c.c. portions, each containing 0.02 gram of tin, are treated with 30 c.c. of concentrated hydrochloric acid. The solution, after dilution to about 150 c.c. with water, is oxidised with 1 gram of permanganate and then treated as indicated below in the case of the actual estimation; 0.02 divided by the number of c.c. of iodine used in the titration gives the amount of tin corresponding to 1 c.c. of the standard iodine solution.

Method of Procedure.—Two grams of the wolfram ore, ground to pass through a 200-mesh sieve, and 7 grams of potassium pyrosulphate are fused in a silica dish. When fusion is complete, in about ten minutes, the mass is cooled and then dissolved by gentle heating with sufficient 5 per cent. tartaric acid to make the bulk of the liquid up to about 200 c.c. Tin having been precipitated with hydrogen sulphide, the residue and the precipitate are collected on an ashless paper, washed three times with hot tartaric acid solution and once with hot water, dried, and ignited in a small silica or platinum crucible.

During this process, a little zinc oxide is sprinkled on the bottom of a porcelain crucible of 15 c.c. capacity and covered with 2 grams of zinc filings. The ashed filter is mixed with zinc oxide and transferred to the crucible. A covering layer of zinc oxide and a few pieces of zinc is added. The total amount of zinc oxide required is about 0.5 gram.

The charged crucible, covered with an inverted lid, is introduced into the furnace, previously heated to 1000° , and is maintained at this temperature for ten minutes. When cold, the lid is prised off and the contents of the crucible are treated with about 30 c.c. of concentrated hydrochloric acid, 1 gram of potassium permanganate, and 10 grams of sodium chloride. The liquid is gently heated until the greater part of the chlorine has been expelled and then boiled for fifteen minutes.

The bulk of the liquid at this stage ought to be 150 to 200 c.c. Ten grams of antimony fragments are added and a small funnel containing two or three pieces of clean marble is inserted in the

neck of the flask. The liquid is boiled for twenty minutes after the colour of the ferric chloride has disappeared, a small piece of marble is added, and the mixture rapidly cooled and titrated with the standard $N/100$ -iodine after the addition of 2 c.c. of starch paste.

A control experiment requires about 2 c.c. of the standard solution.

When 2 grams of ore are taken for assay, the percentage of tin is given by the expression $100nf/2$, where n is the number of c.c. of standard iodine solution required in the titration, and f is the amount of tin corresponding to 1 c.c. of the standard iodine.

Results.—The following table shows a comparison of results obtained by the original method (Powell's) and by the modification described above; the samples were obtained from different Chinese mines.

Sample.	Powell's method.	Modified method.	Sample.	Powell's method.	Modified method.
1	0.04	0.03	5	0.48	0.53
2	0.12	0.09	6	0.58	0.60
3	0.26	0.28	7	0.77	0.79
4	0.32	0.33	8	0.85	0.82

The results, which are the average of two estimations in each case, agree very closely except in the case of sample 5.

Antimony as Reducing Agent.—Antimony, the use of which as a reducing agent is well known, may replace with advantage the granulated lead employed in Powell's method.

The following table shows the results obtained.

Sample.	Reduction with lead.	Reduction with antimony.
1	0.46	0.43
2	0.35	0.31
3	0.76	0.70
4	1.00	1.02

The reduction with antimony, except in case 4, gives lower results. This is attributed to the clearer solution obtained by the antimony reduction which enables the end-point to be perceived more sharply and therefore at an earlier stage.

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[Received, December 11th, 1922.]

CLXV.—*The Swelling of Agar-agar.*

By FRED FAIRBROTHER and HAROLD MASTIN.

A STUDY of the treatment of swelling in many text-books leaves the impression that, as regards its swelling in aqueous solution, agar-agar is affected by acids and by alkalis in much the same manner as gelatin, the two usually being considered together. Hatschek ("Laboratory Manual of Elementary Colloid Chemistry," p. 50), under the preparation of an agar-agar sol, states, "A small addition—one part in 500—of acetic acid is usual and promotes imbibition, but is not essential." Bechold ("Colloids in Biology and Medicine," New York, 1919, p. 67) states, "*The influence of electrolytes on the swelling of gelatin, agar, pig's bladder, cartilage, and fibrin is very considerable. . . . It may in general, be stated that acids and alkalis increase the swelling capacity to an extraordinary degree*" (italics in original).

The classical work on the swelling of agar-agar was carried out by Hofmeister (*Arch. exp. Path. Pharm.*, 1890, **27**, 395), who, however, only examined the action of salts. The matter has also been studied from a botanical point of view by MacDougal and Spoehr (*Proc. Amer. Phil. Soc.*, 1920, **59**, 150), by MacDougal (*ibid.*, 1921, **60**, 15), and by Jochems (*De Imbibitie van plantaardige Celwanden in Oplossingen van Electrolyten*, Diss., 1919, Amsterdam). Both workers found that, in general, acids and alkalis decreased the swelling, but MacDougal and Spoehr employed only a few different concentrations of each acid, and Jochems used commercial agar-agar, which was not subjected to any process of purification. In neither of these cases can the matter be considered to have been exhaustively treated from the physicochemical point of view.

As it seemed highly improbable that agar-agar, largely carbohydrate in composition, could behave in a similar manner as a protein, its degree of swelling in acids and in alkalis has been examined, and the effect of the nitrogen-containing constituent determined. The results show that agar-agar is very sensitive to the action of acids and alkalis, but contrary to the case of gelatin, the swelling is very considerably repressed. Moreover, the small amount of nitrogenous matter plays an insignificant part in the swelling of agar-agar, which behaves essentially as an acid, forming salts, which are ionised in solution, but to what degree has not yet been determined. It is not amphoteric like a protein.

The Chemical Constitution of Agar-agar.

As in the case of gelatin, the swelling of agar-agar can best be considered in the light of its chemical constitution. It is usually

referred to as δ -galactan. It is a hemicellulose, which on hydrolysis with dilute acids gives chiefly *d*-galactose; other hexoses and smaller amounts of pentoses are formed at the same time.

The ash content of agar-agar is high, as shown by the numerous analyses of Fellers (*J. Ind. Eng. Chem.*, 1916, **8**, 1128). Samec and Ssajević (*Compt. rend.*, 1921, **173**, 1474) found that after three months' dialysis, agar-agar still contained inorganic constituents in considerable quantity. Pauli (*Pflüger's Archiv*, 1897, **67**, 219) and MacDougal (*loc. cit.*) claim to have used practically salt-free or ashless agar-agar, but do not give estimations of the ash.

The ash consists chiefly of calcium sulphate, with a small amount of magnesium sulphate and traces of other salts and silica. The behaviour of agar-agar on dialysis and the composition of its ash suggest a similarity between its chemical structure and that of one constituent of carrageen (*Chondrus crispus*). Haas (*Biochem. J.*, 1921, **15**, 469) has shown that the ash content of carrageen cannot be reduced by dialysis below 14.6 per cent. The ash is principally calcium sulphate. In solutions of the original carrageen, calcium ions are present, but not sulphate ions. On ashing, only one-half of the sulphate is found in the ash, the rest being lost as sulphuric acid. This free acid causes blackening when carrageen is heated for some time at 100°. Haas concludes that the calcium and the sulphate are integral parts of the carrageen molecule, and are present as a sulphuric ester, $R\langle\begin{smallmatrix} O-SO_2-O \\ O-SO_2-O \end{smallmatrix}\rangle Ca$. Neuberg and Ohle (*Biochem. Z.*, 1921, **125**, 311), examining the sulphur content of agar-agar, found that the sulphur present in its ash was less than one-half of the total sulphur of the original agar (estimated by fusion with sodium carbonate and potassium nitrate). The quantity of sulphur obtained as sulphuric acid on boiling with hydrochloric acid (strength not stated) for varying periods of time was little greater than that obtained in the ash. Their results are not very concordant. They conclude that the sulphur in agar-agar may be partly present in a form other than that of a sulphuric ester.

The present work was almost completed when a paper appeared by Samec and Ssajević (*Koll. Chem. Beihefte*, 1922, **16**, 285) in which the authors, chiefly from a consideration of the increase of the electrical conductivity and the dialysable fraction of agar-agar on prolonged heating, conclude that it contains an ester of sulphuric acid and possibly of silicic acid. They state that the free acid is monobasic, and give to it the formula $(C_6H_{10}O_3)_{54}SO_4H$.

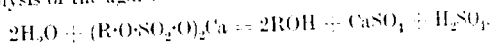
The present work indicates that agar-agar contains, probably as its chief constituent, a sulphuric ester of calcium, and small quantities of the magnesium and other salts. The results obtained

on hydrolysis with hydrochloric acid do not agree with those of Neuberg and Ohle. The following estimations were carried out on strip agar-agar, which was cut up into small pieces about one-eighth to one-quarter of an inch long, in order to obtain samples as uniform as possible, but the results show that, even so, the sampling was not perfect. Samec and Ssajević refer to the difficulty of obtaining concordant results, and probably the lack of concordance in Neuberg and Ohle's figures is attributable to the same cause.

The values given are calculated on the original air-dried agar. The moisture content was 22.6 per cent. (estimated by drying at 105°).

Percentage of SO ₄ in agar-agar.			
	In ash.	2 Grams heated with 100 c.c. of 10% HCl at 100° for 6 hours.	Total sulphur by Benedict's method (oxid. with KClO ₃ and CuSO ₄).
I.	1.43	2.61	2.75
II.	1.40	2.58	2.79

That is to say, nearly the whole of the total sulphur appears as sulphuric acid on hydrolysis with dilute hydrochloric acid. Similar results were obtained with various other batches of agar-agar. In agreement with the workers mentioned above, the agar sol was found to contain calcium-ions, but no sulphate-ions. On heating, however, sulphate-ions were formed, probably as a result of the hydrolysis of the agar:



This breaking down of the agar takes place with great readiness in the presence of even dilute acids. The heating for thirty minutes at 100° of a 2 per cent. sol. 0.01N with respect to hydrochloric acid, destroys its gelling power, and produces free sulphuric acid. Hydrolysis occurs slowly even in distilled water at the ordinary temperature.

The calcium in the agar-agar may be replaced by other metals. An agar-agar sol was heated with a slight excess of potassium oxalate, filtered, and allowed to cool. The gel was cut up and dialysed to remove soluble salts. The product contained practically no calcium or magnesium, but the ash consisted almost entirely of potassium sulphate, the amount of which was approximately equivalent to the amount of calcium sulphate obtained from the original agar-agar. The sol filtered very easily and set to a firm gel.

Attempts were made to prepare the free acid $\text{R}\cdot\text{O}\cdot\text{SO}_2\cdot\text{OH}$ by soaking agar-agar in dilute hydrochloric acid (0.01N) and water

alternately. Under these conditions, a gel was obtained which was almost ash-free (the silica remained), but which could not be melted without hydrolysis occurring, with the consequence that it did not set to a gel again on cooling. This was probably the free acid, which is much less stable than its salts. Samec and Ssajevič state that their electro-dialysed agar-agar was very sensitive and decomposed easily.

EXPERIMENTAL.

The agar-agar used was the best strip obtainable. The strips were cut into pieces 1 in. to 2 in. long and thoroughly mixed. The swelling experiments were all carried out on one batch of agar-agar, the analysis of which was as follows: in the original agar-agar, moisture = 25.2, nitrogen = 0.25, ash = 3.51; after purification, nitrogen = 0.15, ash = 1.25 per cent. The ash and the nitrogen are calculated on the weight of agar-agar dried at 105°.

Purification.—The methods of purification used by previous workers depend mainly on precipitation from a filtered solution of washed agar, by alcohol or acetone, and desiccation of the product. MacDonal (*loc. cit.*) dialysed a hot filtered solution of agar-agar for ten days, poured it into a large volume of acetone, and dried the product with alcohol and ether; the product was stated to contain only traces of nitrogen and ash. Klostermann (*Z. Hyg. Infekt.-Krankh.*, 1921, **94**, 262) has obtained nitrogen-free agar-agar by hydrolysis with alcoholic potash. He states that the carbohydrate part is unaffected, whilst the protein is hydrolysed. For the present purpose, however, this method is undesirable, since we have found that even dilute alkali is not without effect on the chemical composition of agar-agar. More recently, Pekelharing (*Proc. K. Akad. Wetensch. Amsterdam*, 1922, **30**, 309) found that the nitrogen content of agar-agar can be reduced from 1.6 to 0.39 per cent. by heating a solution at about 50° for twenty-four hours, and filtering through wadding. He explains the reduction by supposing that the heating coagulates the protein matter, which is then filtered out.

All successful methods of purification involve washing and filtration, and it would appear that these processes account for the greater part of the purification. Direct experimental confirmation of these points was obtained. Ten grams of an agar-agar (B) which contained 0.41 per cent. of nitrogen (calculated on the weight of the dried product) were soaked in distilled water, which was frequently changed. The first 700 c.c. extracted 16.5 per cent. of a (dry) material very similar to agar-agar in appearance. This material, dried at 105°, contained 0.82 per cent. of nitrogen. A

further 550 c.c. of water extracted only 4.7 per cent. of (dry) material. These results are in agreement with those of previous workers (König and Bettels, *Z. Nahr. Genussm.*, 1905, 10, 457; Fellers, *Soil Sci.*, 1916, 2, 255). Also, some unpublished results of the present authors on the solubility of strip agar-agar in water and dilute acids show a distinct minimum in 0.002*N*-hydrochloric acid, the curve being similar to that of gelatin, indicating that the soluble matter is, partly at any rate, protein in nature.

Commercial agar-agar is contaminated by a considerable amount of foreign matter such as crude fibre, diatoms, sponge spicules, etc. The crude fibre is rich in salts and nitrogen, and consequently simple filtration reduces the nitrogen and ash contents relatively more than dialysis.

A 5 per cent. sol of agar-agar (B) was melted in a tall beaker and allowed to cool slowly so that the crude fibre settled on the bottom. It was found that the upper part of the agar-agar contained only 0.37 per cent. of nitrogen, whilst the lower layer, including the crude fibre, contained 0.81 per cent. of nitrogen.

The ash content of another sample of agar-agar was reduced from 4.72 to 3.25 per cent. by filtration alone. Two weeks' dialysis of agar-agar (B) and filtration reduced the nitrogen from 0.41 to 0.16 per cent. and the ash from 4.99 to 2.38 per cent. (The values are all calculated on the weight of the agar-agar, dried at 105°.)

In the present work the agar-agar was treated as follows. Fifty grams of strip agar were dialysed against running tap water for twenty-one days; the addition of a preservative such as thymol was unnecessary, no trace of mould being formed. The washed strips were made up to 1,000 grams with water and heated in an autoclave at 120° for half an hour. After filtration, an operation generally requiring one or two hours, the clear solution, allowed to cool to about 50°, was poured into a mould, formed on a levelled sheet of plate glass by four thick glass strips which were ground to fit closely at the corners. The plate thus formed, on cooling, was about 20 cm. square by 0.5 cm. thick. Disks 3.4 cm. in diameter were then cut out by means of a sharp cork borer. These were soaked in several changes of distilled water and were then dried, with frequent turning, on glass plates in an incubator at 26°, containing a large dish of calcium chloride and a small electric fan. The fan greatly accelerated the rate of drying and thus prevented the formation of mould, which appeared on slower drying. Desiccation was also much more uniform, and the disks contracted more in thickness than in diameter on drying.

Reaction of Swelling Media.

During recent years, prominence has been given to the effect of the hydrogen-ion concentration on the swelling and other properties of protein gels. The reaction of all the solutions used in these experiments has been determined, and is expressed in Sørensen's notation (p_H); this method facilitates the graphical representation of the results over the wide range of concentrations used. In the more concentrated solutions, the hydrogen-ion concentration was determined by means of the hydrogen electrode. When the solution was very dilute, however, its electrical resistance rendered the usual electrometric technique impracticable; in these cases, the reaction was determined by the indicator method, using for comparison purposes buffer solutions which had been checked against the hydrogen electrode. The latter method is open to question, both on the ground of the effect of the indicator on the reaction of a dilute unbuffered solution, and of the uncertainty of the effect on the colour of the indicator, of the much greater salt concentration in the comparison buffer solution. Control experiments, however, using dilute solutions of known concentrations, similar to those used in the experiments, showed that it was possible to estimate the reaction of even the weakest solutions, with an error generally of less than 0.2 p_H .

In Table II, under "Initial p_H ," are given the values determined experimentally just before the agar-agar disks were put into the solutions. The "Final p_H " values were determined under similar conditions at the end of the swelling time. In the case of the alkali solutions, particularly the more dilute, the initial p_H does not agree with that calculated from the strength of the alkali, assuming the latter to be pure. This may be explained by the unavoidable contamination with carbon dioxide during the manipulation of the solutions and agar-agar disks.

Estimation of Swelling.

The degree of swelling was determined by Hofmeister's original method. Weighed disks were allowed to swell in 200 c.c. of liquid in glass-stoppered jars, in an electrically controlled thermostat oven at 20°. Except in the experiments on the velocity of swelling, the disks were allowed to swell for three days. In view of the fact that in water and in dilute solutions, agar-agar continues to take up water for many weeks, a longer swelling time than three days might be considered advisable; but taking into account the magnitude of the other unavoidable experimental errors, there is no reason to suppose that such a procedure would materially affect the

relative swelling, since the velocity of absorption of water in the different liquids is, after the first few days, approximately proportional to the swelling. The swollen disks were removed by a section lifter, rapidly dried with filter-paper, and transferred to a stoppered weighing bottle. The disks were not damaged by the handling, as is shown by the smoothness of the curves of velocity of swelling. It was not found necessary to add any preservative to the solutions.

In accordance with the experience of workers who have investigated the swelling of gelatin, it was found that the previous history of the gel markedly affected its power of swelling. In particular, the time of heating during sol formation and filtration influenced the subsequent swelling of the gel. Samec and Ssajević (*loc. cit.*) showed that the effect on the degree of dispersion of agar-agar (as measured by the osmotic pressure) of heating at 120° was comparatively small during the first three hours, and that on further heating (three to five hours) the dispersion increased rapidly. The effect on the swelling of the gel of heating at 120° is similar. Heating for several hours causes a decrease in the amount of swelling in pure water and dilute solutions, the percentage swelling in the more concentrated solutions being affected to a somewhat less degree. Disks, the preparation of which from the same lot of agar-agar differed only in the time the sol had been kept at 100° awaiting casting, swelled to different extents in pure water; those which were cast last swelled least. This is the chief reason for the differences in the percentage swelling in water shown in the tables. Prolonged dialysis of the agar-agar tended to have the same effect, in a less degree, as heating, on account of the partial hydrolysis of the agar-agar.

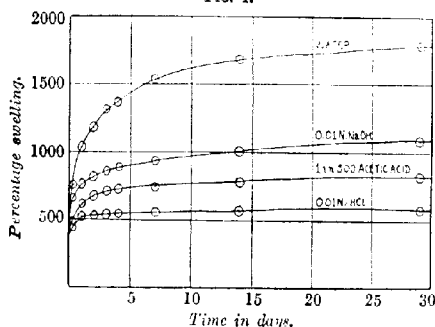
In the following tables are given the degrees of swelling of agar-agar purified by dialysis and filtration. In Table I are given the amounts of water absorbed per cent. of dry agar-agar, in water, 0.01N-hydrochloric acid, 0.01N-sodium hydroxide, and acetic acid (1 in 500), for varying periods. These figures are plotted in Fig. 1. In Table II are given the degrees of swelling of agar-agar in several acids and alkalis. Under "Percentage swelling" are stated the amounts of water absorbed per cent. of dry agar-agar, to the nearest five units. In consequence of the above-mentioned fact, that very slight changes in the thermal history of the agar-agar affect the degree of swelling, the amount of water absorbed is also expressed in Table II as "Relative swelling" in terms of the amount taken up in pure water, which is given as 100. In any series, including the series in Table I, the agar-agar disks were all prepared at the same time and treated alike throughout. Nevertheless, as can be

seen, occasional values (which are enclosed in brackets in the table) were obtained which do not lie on the curve given by the majority. These occur chiefly in the more dilute solutions, in which the reaction of the medium was more affected by the agar-agar itself and by absorption of carbon dioxide.

TABLE I.
Velocity of Swelling.

Time in days.	Water absorbed per cent. of dry agar-agar.							
	$\frac{1}{2}$	1	2	3	4	7	14	29
Water	760	1034	1179	1304	1362	1530	1690	1778
0.01N-Hydrochloric acid	467	523	525	535	544	553	558	565
0.01N-Sodium hydroxide	661	760	808	855	887	940	1000	1085
Acetic acid (1 in 500)	490	607	671	706	723	744	789	812

FIG. 1.



On swelling, the pale brown colour of the disks disappears and they become white and opalescent, in contrast to gelatin, which becomes transparent and almost indistinguishable from the liquid. The surfaces in contact with the glass, during casting, and with the air, respectively, do not dry quite in the same way, and the various phases are reproduced in the reverse order during swelling. A cylinder with concave and convex ends is the usual form. By the third day, when the greater part of the swelling has taken place, the disks will have assumed their final shape; if the swelling is sufficient to restore their original concentration, their appearance will be exactly as it was when they were stamped out.

The relative swelling is plotted against the final p_H in the cases of hydrochloric acid, sodium hydroxide, and barium hydroxide on the graph (Fig. 2). The swelling decreases continuously in hydrochloric acid, almost as a linear function of the negative logarithm

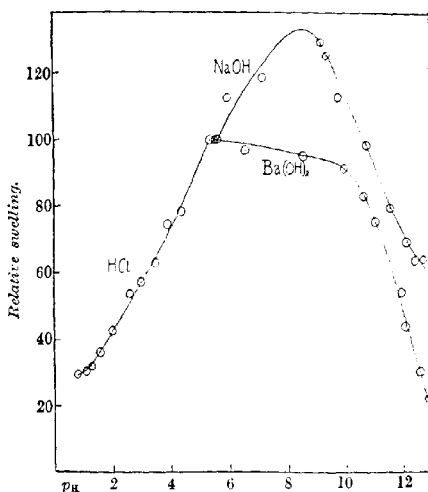
TABLE II.—The Variation of Swelling of Agar-agar in Solutions of Different Concentrations.

Water.	2500'	N.	N.	1280'	640'	N.	320'	N.	N.	800'	N.	400'	N.	100'	50'	25'	12.5'	6.25'
Approx. initial concentration.																		
Initial <i>p</i> _H	5.3	4.6	4.0	3.6	3.3	3.3	3.3	3.8	3.8	2.9	2.6	2.6	2.0	2.0	1.7	1.4	1.1	0.9
Final <i>p</i> _H	5.4	4.8	4.4	3.9	3.5	3.5	3.5	3.0	3.0	3.0	2.6	2.6	2.0	2.0	1.6	1.3	1.1	0.8
% Swelling	125	1405	1115	1060	900	900	63.0	815	805	815	765	765	605	605	510	400	435	425
Relative swelling ...	100	99.0	78.5	74.5	63.0	63.0	—	57.0	57.0	57.0	53.5	53.5	42.5	42.5	36.0	32.0	30.5	29.5
Hydrochloric acid.																		
Initial <i>p</i> _H	5.6	4.0	4.5	4.2	4.2	4.0	4.0	3.8	3.8	3.6	3.5	3.5	3.1	3.1	3.05	3.0	2.9	—
Final <i>p</i> _H	5.7	5.2	5.0	4.7	4.7	4.3	4.3	4.0	4.0	3.8	3.6	3.6	3.2	3.1	3.0	2.9	2.9	—
% Swelling	1150	955	1005	895	895	890	890	805	800	800	745	745	720	720	715	710	745	—
Relative swelling ...	100	83.0	87.0	77.5	77.5	77.0	77.0	69.5	69.5	69.5	64.5	64.5	62.5	62.5	62.5	62.0	64.5	—
Sulphuric acid.																		
Initial <i>p</i> _H	5.4	4.4	4.1	3.7	3.3	3.3	3.3	3.0	2.8	2.8	2.6	2.6	2.0	2.0	1.8	1.5	1.3	—
Final <i>p</i> _H	5.6	4.6	4.2	3.8	3.4	3.4	3.4	3.1	3.0	3.0	2.6	2.6	2.0	2.0	1.8	1.5	1.2	—
% Swelling	900	780	715	675	690	690	640	655	655	655	635	635	515	515	470	425	390	—
Relative swelling ...	100	79.0	72.0	68.0	69.5	69.5	65.0	66.5	66.5	66.5	64.0	64.0	52.5	52.5	47.5	42.5	39.5	—
Oxalic acid.																		
Initial <i>p</i> _H	5.6	4.8	4.1	3.0	3.0	3.6	3.6	3.3	3.0	3.0	2.8	2.8	2.4	2.4	2.0	1.7	1.5	—
Final <i>p</i> _H	5.4	5.0	4.6	4.1	3.8	3.4	3.4	3.4	3.0	3.0	2.8	2.8	2.6	2.6	2.0	1.8	1.6	—
% Swelling	1235	980	1025	965	880	770	880	770	800	800	775	775	635	635	535	520	490	—
Relative swelling ...	100	79.5	83.0	78.0	71.5	62.5	62.5	65.0	65.0	65.0	63.0	63.0	51.5	51.5	43.5	42.0	39.5	—
Phosphoric acid.																		
Initial <i>p</i> _H	5.5	5.0	4.8	4.6	4.0	4.0	4.0	3.6	3.3	3.3	3.0	3.0	2.6	2.6	2.3	2.1	1.9	—
Final <i>p</i> _H	5.7	5.3	5.2	4.8	4.2	4.2	4.2	3.8	3.4	3.4	3.1	3.1	2.6	2.4	2.4	2.15	1.85	—
% Swelling	1240	1125	1215	1135	1030	855	855	855	800	800	745	745	700	700	565	540	565	—
Relative swelling ...	100	91.0	97.5	91.5	83.0	69.0	69.0	69.0	69.0	69.0	64.5	64.5	60.0	60.0	56.5	54.0	45.5	—
Sodium hydroxide.																		
Initial <i>p</i> _H	5.2	6.2	8.4	9.8	10.4	10.4	10.4	10.4	11.3	11.3	11.8	11.8	12.1	12.1	12.3	12.6	12.8	—
Final <i>p</i> _H	5.5	6.6	8.6	9.2	9.4	9.8	9.8	10.3	10.3	10.8	11.6	11.6	12.2	12.2	12.5	12.5	12.8	—
% Swelling	127	1445	1625	1660	1605	1445	1445	1615	1615	1615	1270	1270	985	985	680	620	825	—
Relative swelling ...	100	132.5	118.5	129.0	125.0	112.5	112.5	126.0	126.0	126.0	98.5	98.5	75.3	75.3	69.0	64.0	64.0	—
Barium hydroxide.																		
Initial <i>p</i> _H	5.4	8.0	9.6	10	10.7	10.7	10.7	10.7	11.2	11.2	11.4	11.4	12.0	12.0	12.2	12.5	12.8	—
Final <i>p</i> _H	5.6	6.6	8.6	9.4	9.4	9.4	9.4	10.7	10.7	11.0	11.7	11.7	12.5	12.5	12.7	13.0	12.9	—
% Swelling	100	99.5	99.0	123.5	123.5	123.5	123.5	83.0	83.0	74.0	74.0	74.0	55.0	55.0	43.6	39.2	22.0	—
Relative swelling ...	100	99.5	99.0	123.5	123.5	123.5	123.5	83.0	83.0	74.0	74.0	74.0	55.0	55.0	43.6	39.2	22.0	—

of the hydrogen-ion concentration. The values for the relative swelling in acetic, sulphuric, oxalic, and phosphoric acids, when plotted, lie close to the hydrochloric acid curve, the relative swelling at a given value of p_H being of the same order in each of the acids. There is no evidence that the relative swelling at a given p_H is any less in sulphuric acid than in the other acids, as was found by Loeb (*J. Gen. Physiol.*, 1920, 3, 247) to be the case for gelatin.

On the other hand, in sodium hydroxide solution the relative swelling shows a maximum, greater than the maximum swelling in water. This may be due in some degree to the fact that the water

FIG. 2.



was always slightly acid owing to absorption of carbon dioxide, and also to partial replacement of the calcium in the agar-agar, by sodium. An agar disk, when allowed to swell in 0.01N-sodium hydroxide and in water alternately, for a number of changes, swelled more than in either separately, and a subsequent analysis showed that the calcium had been entirely replaced by sodium.

The swelling is depressed in baryta solutions, but in view of the difficulty of excluding all contamination with carbon dioxide, one cannot say if in all cases the swelling is less than in water. Only in one case, in several series of experiments on the swelling in baryta solution, did the disks in the dilutest solutions swell somewhat more than in the corresponding water solutions. There is no

doubt, however, that agar-agar swells to a much less degree in dilute baryta than in sodium hydroxide solution of the same concentration or p_H .

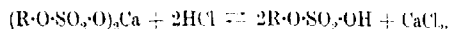
The relative swelling in dilute ammonia showed a pronounced maximum, greater than that in sodium hydroxide solution, but lying at about the same p_H . Owing to the difficulty of measuring the p_H of more concentrated ammonia solutions, a complete series of experiments was not carried out.

Agar-agar from which the nitrogen had been further removed by tryptic digestion showed no difference from agar-agar treated as above, as regards swelling in acid or alkali. This demonstrates the small part which the remaining nitrogenous constituent plays in the swelling.

Also agar-agar of the same batch, made up into a sol and cast into disks without dialysis or filtration, showed qualitatively the same decrease of swelling in acids, although in consequence of the shorter time taken in its preparation, the disks in each case swelled to a greater extent.

Conclusion.

Agar-agar appears to consist principally of the calcium salt of an acid sulphuric ester, $(R \cdot O \cdot SO_2 \cdot O)_2Ca$. The effect of acid is to produce a reversible equilibrium of the type



the calcium salt and the free acid sulphuric ester being ionised to some extent. The free acid swells less in water than the calcium salt, and its ionisation and swelling are further diminished by the presence of acid. When an agar-agar disk is allowed to soak alternately in water and in dilute hydrochloric acid (0.01N), the calcium is almost entirely removed. The swelling of the product is much less in water than that of the calcium salt, is decreased by acids, and shows a maximum in dilute alkali solution.

When agar-agar is heated with dilute alkali solution, it darkens in colour, particularly with ammonia, which blackens it very quickly. The brown substance produced by caustic soda can be entirely washed out in a few days by dialysis. The darkening is not due to free sulphuric acid, for the addition of acid of a greater concentration than could possibly be produced by hydrolysis of the agar causes no darkening on boiling.

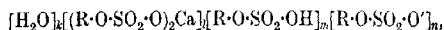
The theory that the swelling of agar-agar is principally governed by the chemical behaviour of the sulphuric ester is supported by the results of Kruyt and Jong (*Z. physikal. Chem.*, 1922, 100, 250), who obtained stoichiometrical relationships for the effect of different kations on the viscosity of agar-agar sols. They state

“ Wir haben nun ausführliche Untersuchungen am Agarsol angestellt, das ein höheres Kohlenhydrat und deshalb keinesfalls ein Elektrolyt ist, dennoch aber ein typisches lyophiles Sol liefert.” Owing to this assumption, they had some little difficulty in explaining their results, which follow at once from the present theory.

Further evidence in support of the foregoing theory of the composition of an agar-agar gel is afforded by its behaviour as an electro-osmotic diaphragm. Several workers have observed that no reversal of the direction of flow takes place when the diaphragm is acidified. This has been confirmed, and the explanation follows immediately from the above theory. In the neutral state, the micellæ consist of undissociated salt and sulphuric ester-ion, both possibly polymerised, $[H_2O]_k[(R \cdot O \cdot SO_2 \cdot O)_2Ca]_l[R \cdot O \cdot SO_2 \cdot O']_m$.

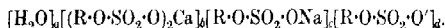
The calcium-ions exist in the intermicellar spaces. On applying an external electromotive force, the water will move to the cathode.

When acid is added, the calcium is partly replaced by hydrogen so that the composition of the micellæ will be



that is, the product will still be electronegative.

In the presence of alkali, the calcium is partly replaced by the alkali metal, and the micellæ will consist of



Through all these changes the colloid complex remains negatively charged with respect to the water, and therefore the direction of electroendosmosis will be towards the cathode.

Summary.

1. Agar-agar consists principally of the calcium salt of an acid sulphuric ester, which is considered to be ionised in the sol and the gel states.
2. The corresponding potassium salt and the free acid have been prepared. The potassium salt forms a very firm gel. The free acid decomposes readily on heating.
3. Agar-agar has been purified by dialysis and filtration, and the degree of swelling of the purified agar-agar in various solutions has been determined.
4. Agar-agar behaves quite differently from gelatin as regards its swelling in acids and alkalis.
5. Acids decrease the swelling, which is nearly proportional to the p_H of the solution. The effect of hydrochloric, sulphuric, oxalic, acetic, and phosphoric acids is almost the same at the same p_H .
6. Agar-agar swells more in very dilute caustic soda solution

than in water; in more concentrated alkalis the swelling is less than it is in water. Agar-agar swells much less in baryta solutions than in water.

7. These results support the view that the swelling of agar-agar is governed by the chemical reaction between the medium and the sulphuric ester.

8. The behaviour of agar-agar as an electroendosmotic diaphragm further supports the theory that the framework of an agar-agar gel consists of hydrated undissociated sulphuric esters and the electronegative sulphuric ester complex.

The authors beg to thank the Department of Scientific and Industrial Research for a grant to one of them (H.M.) which enabled part of the above work to be carried out.

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[Received, March 19th, 1923.]

CLXVI.—*The Action of Sulphuryl Chloride on Organic Substances. Part II.*

By THOMAS HAROLD DURRANS.

THE action of sulphuryl chloride on more complex benzenoid substances than the simple mono-substituted derivatives of benzene previously investigated (T., 1922, **121**, 44) has been examined under the conditions of experiment therein laid down, except where otherwise stated.

The table shows briefly the results obtained.

Organic substance.	Products.
Benzyl benzoate.	Benzyl chloride. Benzoic acid.
Benzyl acetate.	Traces of acetic anhydride and benzoic acid.
Benzil.	No action.
Anisole.	2 : 4 : 6-Trichloroanisole.
Salicylaldehyde.	5-Chlorosalicylaldehyde.
Anisaldehyde.	3 : 5-Dichloroanisaldehyde.
Cinnamaldehyde.	<i>α</i> , <i>β</i> -Dichloro- <i>β</i> -phenylpropionaldehyde.
Cinnamic acid.	<i>α</i> , <i>β</i> -Dichloro- <i>β</i> -phenylpropionic acid.
Anthranilic acid.	3 : 5-Dichloro-2-aminobenzoic acid.
Anethole.	A tetrachloroanethole.
Methylchavicol.	A tetrachloromethylchavicol.

The positions of the chlorine atoms in the last two products have not yet been satisfactorily defined.

EXPERIMENTAL.

Benzyl Benzoate.—Sulphuryl chloride (5 mols.) was distilled on to benzyl benzoate (m. p. 19°; 1 mol.); very little sensible reaction

took place. After three days, the excess of sulphuryl chloride having been removed by distillation, the remaining liquid gave two main fractions and a black residue; the small, first fraction, distilling up to $80^{\circ}/15$ mm., was identified as benzyl chloride, the second fraction, b. p. 140° — $190^{\circ}/15$ mm., as benzoic acid.

It is probable that benzoic anhydride is one of the products of the reaction, but the low vapour pressure of this substance (b. p. 360°) necessitates for its distillation a temperature which, in presence of traces of sulphur trioxide, is favourable to decomposition, water, and therefore benzoic acid also, being produced.

Benzyl Acetate.—A mixture of sulphuryl chloride (4 mols.) and benzyl acetate (1 mol.) was gently boiled under reflux for about eight hours and then fractionally distilled. After removal of the excess of sulphuryl chloride, two fractions were taken boiling approximately at $48^{\circ}/12$ mm. and $95^{\circ}/10$ mm., the second being comparatively large. The first fraction boiled under atmospheric pressure at 118° , the temperature rising rapidly to 135° , and had all the characteristics of acetic anhydride. The second fraction, b. p. 212° — $216^{\circ}/760$ mm., was unchanged benzyl acetate. The residue remaining from the original distillation gave a sublimate of benzoic acid, m. p. 120° .

Benzyl acetate is, in the main, unattacked by sulphuryl chloride under the conditions of the experiment, only small quantities of acetic anhydride and benzoic acid being produced.

Benzil.—Sulphuryl chloride (7 mols.) was distilled on to benzil (1 mol.), when solution took place with a slight absorption of heat. After three days, the excess of sulphuryl chloride was slowly distilled off, and the residue poured into water. The yellow solid obtained proved to be benzil in almost unchanged amount.

Anisole.—Peratoner (*Gazzetta*, 1898, 28, i. 197) found that *p*-chloroanisole is the product of the reaction between sulphuryl chloride and anisole, while Böeseken (*Rec. trav. chim.*, 1911, 30, 281), using aluminium chloride as a catalyst, obtained a chloroanisole and dianisyl sulphoxide. Hugoumenq (*Ann. Chim. Phys.*, 1890, [vi], 20, 521) obtained a trichloroanisole, m. p. 60.5° , by the action of chlorine on anisole. It has now been found that impure sulphuryl chloride can be made to yield the trichloroanisole of Hugoumenq, probably by virtue of its partial dissociation into sulphur dioxide and chlorine (compare Trautz, *Z. Elektrochem.*, 1908, 14, 534).

Commercial sulphuryl chloride was mixed in large excess with anisole; a solid substance formed which subsequently dissolved in the excess of sulphuryl chloride. The solution was heated under reflux for several hours, and the excess of sulphuryl chloride

then slowly distilled off. The residue was poured into water and after purification melted at 60° (Found: Cl = 50.12. Calc. for $C_7H_5OCl_3$, Cl = 50.36 per cent.). The substance is identical with that obtained by Hugounenq (*loc. cit.*) and is 2:4:6-trichloro-anisole.

Salicylaldehyde.—Sulphuryl chloride (5 mols.) was distilled on to salicylaldehyde (1 mol.). Vigorous reaction ensued, much heat being evolved, and the mixture passed through a series of colour changes, from purple to red, orange, and finally to yellow (compare Silberrad, T., 1921, **119**, 2030). After about half an hour, the mixture solidified. The excess of sulphuryl chloride was distilled off; the residue boiled at about $105^{\circ}/12$ mm. The distillate, crystallised from benzene, gave long, flat needles, m. p. 100° , of 5-chlorosalicylaldehyde, identical with the compound obtained in a similar way by Peratoner (*loc. cit.*, p. 235) (Found: C = 52.53; H = 3.37. Calc., C = 53.67; H = 3.19 per cent.). The crystals, oxidised with chromic acid mixture, gave a small yield of 5-chlorosalicylic acid, m. p. 172° .

Anisaldehyde.—Vigorous action occurred when sulphuryl chloride (9 mols.) was distilled on to anisaldehyde (1 mol.), and the mixture rapidly darkened. After remaining for three days at room temperature, the sulphuryl chloride was slowly distilled off. From the residue was obtained a large fraction, boiling at about $149^{\circ}/11$ mm., which solidified on cooling. The bright red solid, after crystallisation from alcohol, melted at 61.5° , was odourless and colourless, and had the properties of an aldehyde (Found: C = 46.95; H = 2.96; Cl = 34.77. $C_8H_6O_2Cl_2$ requires C = 46.82; H = 2.93; Cl = 34.63 per cent.). Oxidised with chromic acid mixture, it gave an 80 per cent. yield of an acid, m. p. $202-202.5^{\circ}$, which, by the melting point of the mixture, was identified as 3:5-dichloroanisic acid (compare Reinecke, Z. Chem., 1866, 366). On boiling this acid with concentrated hydriodic acid, 3:5-dichloro-4-hydroxybenzoic acid, m. p. 265° (corr.), was obtained (compare Mazzara, Gazzetta, 1899, **29**, i, 388; Tarugi, *ibid.*, **30**, ii, 490; Bertozzi, *ibid.*, **29**, ii, 39).

The 3:5-dichloroanisaldehyde, similarly treated with hydriodic acid, yielded 3:5-dichloro-4-hydroxybenzaldehyde, m. p. 156° , an odourless, white solid (compare Auwers and Reis, Ber., 1896, **29**, 2356).

It is evident that the product of the reaction between anisaldehyde and sulphuryl chloride is 3:5-dichloroanisaldehyde. No dichloro-derivative of anisaldehyde appears to have been previously known.

Cinnamaldehyde.—The reaction between cinnamaldehyde and

sulphuryl chloride was very vigorous, free chlorine being liberated along with sulphur dioxide. The product, obtained in good yield, was a liquid, b. p. 151–153°/20 mm., which would not solidify when cooled to –12° and had a sharp, weak odour reminiscent of ozone. It would not readily yield chlorine to alcoholic silver nitrate solution (Found: C = 52.76; H = 3.79; Cl = 34.88. $C_9H_8OCl_2$ requires C = 53.20; H = 3.94; Cl = 34.97 per cent.). The substance can be readily oxidised with nitric acid, and difficultly with chromic acid mixture, to yield an acid which on hydrolysis with sodium hydroxide solution gives ω -chlorostyrene.

It seems evident that the compound formed by the action of sulphuryl chloride on cinnamaldehyde is $\alpha\beta$ -dichloro- β -phenylpropaldehyde, although the properties of the product obtained as above are not in agreement with those recorded by Naar (*Ber.*, 1891, 24, 246) for this aldehyde. Naar states that it is a crystalline solid which has lachrymatory properties, and gives off hydrogen chloride very readily, thus making accurate analysis difficult.

Cinnamic Acid.—Sulphuryl chloride ($4\frac{1}{2}$ mols.) was run on to cinnamic acid (1 mol.); the acid dissolved, but no reaction was observed. After six weeks, the excess of sulphuryl chloride was removed and the residue poured into water. The solid thus obtained, after purification, melted at 167–168° and was sparingly soluble in carbon tetrachloride or carbon disulphide (Found: Cl = 32.17. Calc. for $C_9H_7O_2Cl_2$, Cl = 32.42 per cent.).

The product, hydrolysed with sodium hydroxide solution, yielded an oil, b. p. 83°/18 mm., having the characteristic hyacinth odour of ω -chlorostyrene (Found: C = 68.65; H = 5.12. Calc., C = 69.31; H = 5.05 per cent.).

From the aqueous alkaline solution remaining after hydrolysis, α -chlorocinnamic acid, m. p. 139°, characterised by its extraordinarily high solubility in many organic solvents, was isolated. This acid is evidently α -chlorocinnamic acid (compare Sudborough and James, T., 1906, 89, 105) (Found: C = 59.16; H = 3.94. Calc., C = 59.17; H = 3.83 per cent.).

The product of the reaction between sulphuryl chloride and cinnamic acid is therefore $\alpha\beta$ -dichloro- β -phenylpropionic acid.

Anthranilic Acid.—Saturated acids are, in general, not acted on by sulphuryl chloride, but the highly basic nature of anthranilic acid causes it to react readily.

Sulphuryl chloride (4 mols.) was distilled on to anthranilic acid (1 mol.). Action commenced immediately and a white solid sublimed. After a short period, the excess of sulphuryl chloride was distilled off, a light bluish-green, insoluble solid remaining. This solid, which was almost completely soluble in sodium hydroxide

solution and was reprecipitated therefrom by acids, crystallised from benzene in needles, m. p. 223° (Found : C = 41.23; H = 2.54; Cl = 33.78. $\text{NH}_2\cdot\text{C}_6\text{H}_2\text{Cl}_2\cdot\text{CO}_2\text{H}$ requires C = 40.77; H = 2.42; Cl = 34.46 per cent.). The substance was converted by recrystallisation from glacial acetic acid into a solid, m. p. 278° , which was probably the acetyl-amino-derivative.

The dichloro-amino-acid boiled at about 260° , prolonged boiling causing the boiling point to decline to about 247° , with evolution of carbon dioxide and formation of 2:4-dichloroaniline (compare Dorsch, *J. pr. Chem.*, 1886, [ii], **33**, 52; Franke, *ibid.*, 1891, [ii], **44**, 432). A substance obtained in small quantity from the original reaction mixture had an olive-green colour, melted at 277° , was insoluble in acids and alkalis and in most organic solvents, and left no ash on ignition. The amount of the substance was too small to allow it to be identified.

The main product of the reaction between sulphuryl chloride and anthranilic acid is therefore 3:5-dichloro-2-aminobenzoic acid.

Since this work was completed, Eller and Klemm (*Ber.*, 1923, **55**, [B], 2177) have obtained first 5-chloro-2-aminobenzoic acid and finally 3:5-dichloro-2-aminobenzoic acid by acting on anthranilic acid with sulphuryl chloride in ethereal solution.

Anethole.—Sulphuryl chloride (6 mols.) was distilled very slowly on to anethole (1 mol.), a very vigorous reaction taking place. After forty-eight hours, the excess of sulphuryl chloride was removed and the residue distilled under diminished pressure. By repeated fractional distillation, a large yield of colourless, nearly odourless, crystalline solid was obtained, m. p. 70.5° , b. p. 191.17 mm. (Found : C = 41.97, 41.50; H = 3.65, 3.38; Cl = 50.1. $\text{C}_{10}\text{H}_9\text{OCl}_4$ requires C = 41.66; H = 3.47; Cl = 49.3 per cent.).

The substance on boiling with alcoholic silver nitrate solution loses one atom of chlorine (Found : loss = 12.45. Calc., loss = 12.32 per cent.).

Boiling with N-alcoholic sodium hydroxide yields a substance, b. p. $164^{\circ}/20$ mm., m. p. 36° , having a very faint odour resembling that of amyl salicylate (Found : C = 47.62; H = 3.58. $\text{C}_{10}\text{H}_9\text{OCl}_2$ requires C = 47.72; H = 3.57 per cent.).

It does not seem possible that this substance can be the trichloro-derivative described by Darzens (*Compt. rend.*, 1897, **124**, 564), although the melting points are similar.

The constitutions of these two substances have not yet been satisfactorily established.

Methylchavicol.—Sulphuryl chloride (4 mols.) was distilled on to methylchavicol (1 mol.), reaction immediately ensuing. After fractional distillation, a liquid was obtained which boiled at $199^{\circ}/13$

mm., but would not solidify even at -15° (Found: C = 41.66; H = 3.47; Cl = 49.57. $C_{10}H_{10}Cl_4$ requires C = 41.53; H = 3.56; Cl = 49.30 per cent.). This tetrachloro-derivative is different from that obtained in a similar manner from anethole and has not yet been identified.

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[Received, April 28th, 1923.]

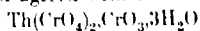
CLXVII.—Investigations of the Chromates of Thorium and the Rare Earths. Part I. The System Thorium Oxide-Chromic Anhydride-Water at 25° .

By HUBERT THOMAS STANLEY BRITTON.

PALMER (*Amer. Chem. J.*, 1895, **17**, 374) was the first to prepare thorium chromate trihydrate. He obtained it by the action of chromic acid on thorium hydroxide and also by the action of a solution of potassium dichromate on one of thorium nitrate. Using potassium chromate, however, he found that the precipitate obtained gradually changed into the crystalline thorium chromate. The only analysis given of such a precipitate was of one which had been obtained by the interaction of potassium chromate and thorium nitrate in the molar proportion of 3:1. This precipitate was dense yellow and when dried at 100° corresponded with the formula $Th(OH)_2CrO_4$. The production of this substance led him to believe that it was the intermediate stage in the formation of the hydrated thorium chromate. Haber (*Sitzungsber. K. Akad. Wiss. Wien*, 1897, [iib], **106**, 690; *Monatsh.*, 1897, **18**, 687) also prepared thorium chromate by using similar methods. He does not seem to have investigated the precipitates formed by the action of neutral alkali chromates on solutions of thorium salts, other than to remark that the precipitates thus obtained were not crystalline. The thorium chromate, when examined microscopically, was found to be in the form of rhombic leaflets. These crystals were insoluble in water, but were soluble in moderately concentrated mineral acids. Moreover, he directed attention to the fact that the salts precipitated from solutions of thorium and zirconium salts by means of solutions of either chromic acid or alkali dichromates were characteristic, as these reagents produced no precipitates from solutions of the cerium and gadolinium earths. Later, Muthmann and Baur (*Ber.*, 1900, **33**, 2028) found that potassium chromate provided an excellent reagent for the purification of commercial thorium nitrate. If a solution of potassium chromate

is dropped carefully into a boiling solution of thorium nitrate, first thorium will be precipitated completely as chromate and afterwards some rare earths begin to appear, indicated by a change in colour of the precipitate. This was the principle of Baur's process (D.R.-P. 120012, 1900).

The relative insolubility of thorium chromate renders it quite a useful compound. The product obtained from the acid solution is finely crystalline and therefore can be easily washed. On the other hand, the precipitate generally obtained by the addition of potassium chromate to solutions of thorium salts is of an extremely variable nature, dependent on both the concentrations and temperature employed. Sometimes it is flocculent and difficult to filter and sometimes granular and easily washed and filtered. These precipitates are basic and appear to have no fixed composition. Under certain conditions, however, it is possible to obtain the normal thorium chromate (*vide infra*). Whereas the precipitation of thorium as basic chromate is complete when sufficient potassium chromate has been added, that of the trihydrate by means of potassium dichromate or chromic acid solution is incomplete and has been found to depend on the acidity of the solutions. Consideration of the solubility product led to the belief that the precipitation of crystalline thorium chromate would be enhanced by increasing the concentration of the chromate-ion. This was found to be true in the case of aqueous solutions of thorium chromate to which potassium chromate had been added. When, however, dichromate or free chromic acid was added, the relatively insoluble thorium chromate became remarkably soluble, especially in the more concentrated solutions of chromic acid. The isotherm at 25° of the system in question was therefore investigated and the explanation of this behaviour was found in the formation of an acid thorium chromate, the composition of which was arrived at by extrapolation by the residue method of Schreinemakers from the phase diagram and agreed with the formula



or $\text{Th} \begin{smallmatrix} < \\ \text{CrO}_4 \end{smallmatrix} \cdot 3\text{H}_2\text{O}$. On referring to the phase diagram, it will be observed that this new compound is decomposed by water. The first formula is obviously the correct one, for the compound can exist only in equilibrium with highly concentrated chromic acid solutions and is consequently an acid salt. No attempt was made to isolate the salt from the mother-liquor.

Because of the slight solubility of thorium chromate, the following work falls into two sections : (1) the solubility of thorium chromate in solutions of chromic acid, and (2) a consideration of the substances

obtained from the interaction of thorium hydroxide and chromic acid when in the respective molar proportion not greater than 2:1, that is, the formation of basic salts, if any.

EXPERIMENTAL.

Preparation of Materials.—For the first part of the work, it was considered better to use as starting material crystalline thorium chromate, instead of thorium hydroxide, since this generally retains adsorbed substances which are extremely difficult to extract. Thorium chromate was crystallised from a boiling solution of thorium nitrate which contained a small excess of either potassium dichromate or chromic acid. High concentrations of the latter reagents gave negligible yields.

The chromic anhydride used was of the "A.R." standard, and was free from sulphuric acid and other acids as indicated by the ordinary tests.

Methods of Analysis.—The chromic acid was estimated by titrating the iodine liberated when excess of potassium iodide had been added in the presence of moderately concentrated hydrochloric acid.

The thorium was estimated by precipitation as oxalate. As was shown by Hauser and Wirth (*Z. anorg. Chem.*, 1909, **22**, 484; *Z. anorg. Chem.*, 1912, **78**, 75), the solubility of thorium oxalate in dilute mineral acids, oxalic acid, and ammonium oxalate solutions may give rise to appreciable errors in the estimation of thorium. Hence before investigating the oxalate method, the precipitation by means of ammonium hydroxide was examined. After one precipitation, the precipitate was yellow and contained much chromate. Even after the precipitate had been dissolved in dilute nitric acid and reprecipitated with ammonia and this process repeated six times, the final precipitate was far from being free of chromate. When dried and analysed, it was found to contain thorium and chromic anhydride in the molar ratio of 1:0.485 and also contained some ammonia and nitrate. Microscopic examination revealed that it was made up of amorphous particles and exceedingly small rhombic crystals. Hydrogen-ion measurements have shown that both thorium hydroxide and the basic chromate of thorium are precipitated at the same hydron concentration. Consequently, in the presence of chromate thorium cannot be estimated by precipitation as hydroxide.

The following method was found satisfactory. The precipitate is dissolved in the minimum amount of dilute hydrochloric acid, a small excess of saturated oxalic acid solution added in the cold, and the mixture boiled until effervescence ceases and the solution

has become green. The precipitate is collected immediately, washed, and ignited. The precipitation is quantitative, much of the oxalic acid having been utilised in effecting the reduction of the chromic acid and then holding the chromium in solution as a complex oxalate. In the case of liquid phases, no hydrochloric acid is, of course, necessary. By boiling, precipitation was found to be complete in a few minutes, and thus there is no reason for keeping over-night, as is often recommended. When precipitated in the cold, the thorium oxalate was free from foreign matter, but when precipitation was effected from boiling solutions there was a distinct tendency for the oxalate to be accompanied by some thorium chromate. The above method is very satisfactory, for much of the excess of oxalic acid which tends to render the precipitation incomplete is destroyed.

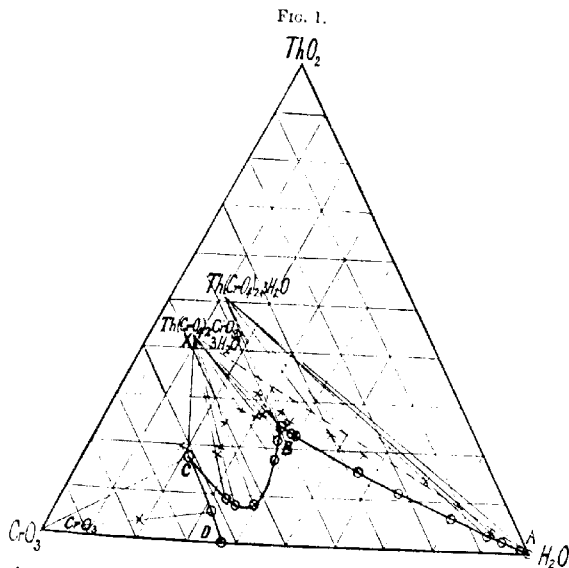
I. *The Solubility of Thorium Chromate in Chromic Acid Solutions.*

Pure crystalline thorium chromate was added to warm solutions of chromic acid of different concentrations in quantities sufficient to saturate them. These solutions were placed in a thermostat, regulated at 25°, and were mechanically stirred for several days until equilibrium had been reached. The solubility of thorium chromate in water was obtained by stirring the crystals with water for a month. The univariant points were obtained by stirring liquid phases, the compositions of which were very nearly those of the required liquid phases, with their respective residues containing the acid chromate, and excess of the other appropriate solid phases. The analyses of the residues refer to those left in the bottles after the liquid phases had been poured off. It was not possible to separate more of the adhering mother-liquor by filtration through filter-paper on account of the chromic acid present. The following table contains the data obtained, which are represented graphically in Fig. 1.

The branch *AB* of the system represents liquid phases in equilibrium with thorium chromate trihydrate as indicated by the point in which the tie-lines intersect. It will be seen that with increasing concentration the relative amounts of chromic acid required to keep the thorium in solution gradually become less until at *B* the liquid phase attains equilibrium with two solid phases—thorium chromate trihydrate and the acid chromate. It is perhaps worth mentioning that the curve *AB* (prolonged) and the $\text{ThO}_2\text{-CrO}_3$ axis intersect at a point which approximately corresponds to the ratio of 1 mol. of ThO_2 to 3 mols. of CrO_3 , which happens to be the ratio in which the two oxides occur in the acid chromate. The section *BC* represents liquid phases in equilib-

TABLE I.

Liquid phases.		Residues.		Solid phases.
Percentages by weight.				
ThO ₂ .	CrO ₃ .	ThO ₂ .	CrO ₃ .	
0.044	0.033	51.00	38.60	Th(CrO ₄) ₂ ·3H ₂ O
0.452	1.376	—	—	" "
2.09	4.58	3.83	5.80	" "
3.08	7.15	14.21	14.63	" "
6.52	13.09	—	—	" "
11.27	21.75	19.35	25.19	" "
15.62	28.00	23.41	29.97	" "
22.87	37.27	25.76	37.21	" "
23.25	37.45	27.57	38.00	" "
24.22	39.49	31.39	40.72	" "
23.04	40.23	26.93	42.22	{ Th(CrO ₄) ₂ ·3H ₂ O and Th(CrO ₄) ₂ ·CrO ₃ ·3H ₂ O Th(CrO ₄) ₂ ·CrO ₃ ·3H ₂ O
21.59	41.56	26.26	43.94	
17.08	44.20	27.71	45.91	
7.91	52.60	24.68	50.78	" "
7.52	56.79	19.64	54.12	" "
9.09	57.57	18.18	55.32	" "
17.65	61.38	19.60	61.98	{ Th(CrO ₄) ₂ ·CrO ₃ ·3H ₂ O and CrO ₃ CrO ₃
6.27	61.84	3.73	77.85	
0	62.87	—	—	
				" "



rium with the compound indicated by the point of intersection of the lines corresponding to the various liquid phases and their

respective residues. This point indicates the composition ThO_2 42.8, CrO_3 48.7, and H_2O 8.7 per cent., as compared with the calculated percentage composition of $\text{Th}(\text{CrO}_4)_2 \cdot \text{CrO}_3 \cdot 3\text{H}_2\text{O}$ — ThO_2 42.76, CrO_3 48.51, and H_2O 8.73 per cent. Microscopic examination of the residue containing the acid chromate showed that the latter was made up of crystals which were square in section, which may have been either the basal section of cubic crystals or a section of tetragonal ones. As the line XA does not intersect the curve BC , the acid salt will be decomposed by water. C represents the liquid phase in equilibrium with the two solid phases—the acid chromate of thorium and chromic anhydride. The liquid phase represented by the point C was extraordinarily viscous and consequently difficult to manipulate. It was almost impossible to eliminate entirely from the liquid phase small suspensions of the solid phases. The values, which had become constant, taken for the liquid phase and its residue are those of analyses made after the phases, having first been stirred for a fortnight, had stood undisturbed for a month.

II. Basic Chromates.

If thorium hydroxide is suspended in a dilute solution of chromic acid, it will be converted gradually into the normal chromate, the change occurring more rapidly on boiling. No basic salt of definite composition has been found. The composition varies, gradually approaching that of the normal chromate, but the conversion is complete only after long boiling. Thus substances which had become apparently crystalline, on analysis were found to be somewhat basic, for example, one sample corresponded to 1 mol. of ThO_2 , 1.8 mols. of CrO_3 , and 3.6 mols. of H_2O , evidently due to some hydroxide having been occluded by the crystals of the normal chromate.

The action of potassium chromate solution on a solution of a thorium salt provides a convenient method of studying the formation of the basic precipitates thereby produced. The precipitates are of variable composition and also the amounts of thorium precipitated depend on the concentrations of the reactants. For example, on mixing 250 c.c. of thorium nitrate solution, containing 2.5 millimols., and 100 c.c. of potassium chromate solution, containing 5 millimols., 59.3 per cent. of the thorium present was precipitated, the precipitate containing thorium oxide and chromic anhydride in the respective molar proportion of 1 to 1.38. An excess of potassium chromate, however, produces almost complete precipitation of the thorium. If the change in the hydrogen-ion concentration during the precipitation of basic thorium chromate

is followed when potassium chromate is added slowly to a solution of thorium nitrate, it will be observed that while those portions of potassium chromate are being added which are insufficient to cause permanent precipitation there will be a gradual diminution in the hydron concentration, until the concentration is reached necessary for the formation of a precipitate.

At this point, further addition of potassium chromate will produce further precipitation, but during the greater part of this process the hydrogen-ion concentration will remain constant. It is important to note that the concentration required for the precipitation of the basic thorium chromate is also that required for the precipitation of thorium hydroxide from solutions of thorium salts of like concentration by means of alkali. (An account of the work on which these statements are based will be published later.) It therefore seems probable that the basic chromates of thorium are really mixtures of thorium hydroxide and thorium chromate. In other words, these basic chromates may be regarded as so-called adsorption compounds, or, taking into account the slight solubility of the normal thorium chromate, as having been produced by the simultaneous precipitation of both the hydroxide and the chromate. The basic chromate which Palmer claims to have isolated is a special case of such a mixture.

In concluding, reference should be made to the behaviour of solutions of thorium salts to which potassium chromate has been added in quantities insufficient to give a permanent precipitate on account of the acid which is liberated by hydrolysis. On standing at room temperature, if the concentration is sufficiently great, crystals of thorium chromate trihydrate will be deposited slowly; but deposition occurs almost immediately from the boiling solution.

The author desires to take this opportunity of recording his thanks to the Chemical Society for a grant from the Research Fund.

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[Received, April 30th, 1923.]

CLXVIII.—*The Propagation of Flame from a Spark in a Closed Tube through a Homogeneous Inflammable Mixture.*

By OLIVER COLIGNY DE CHAMFLEUR ELLIS.

THE experiments described in this paper were begun with the object of studying the progress of flame through an inflammable mixture as it is propagated from a spark near to the closed end of

a tube, the other—or "distal"—end of which is open. For most purposes, however, this proved to be merely a special case of ignition in a tube closed at both ends; that is, a tube open at the distal end may be regarded, with respect to that end, as a closed tube of infinite length. To open or close the *firing* end, on the other hand, is to alter the mode of inflammation.

The propagation of the flame in various horizontal glass cylinders was photographed on a vertically moving film, so that the recorded picture is compounded of the two motions. This is the *méthode photographique* of Mallard and Le Chatelier (*Ann. Mines*, 1883, [viii], 4, 312), perfected by Professor H. B. Dixon (*Phil. Trans.*, 1903, [A], 200, 343), to whom the author is profoundly indebted, not only for the use of his original apparatus, but also for innumerable facilities and invaluable suggestions.

The present investigation has shown that the movement of the flame in any given mixture is dependent on the length and bore of the tube, the position of the spark-gap, the initial mechanical turbulence, the intensity of the spark, and the initial temperature and pressure.

When all these factors have been kept rigidly unvaried, no difficulty has been experienced in the repetition of results. When one factor is varied, the effect on the speed of the flame is similar, as a rule, in all sections of its path. (See, for example, Fig. 4.) The shorter the section used as the basis of calculation, the nearer can the tube be brought to the camera; the slower the section used, the greater is the "exposure" for any given film-speed. Accuracy in the measurement of the flame-speed is dependent on the use of such a film-speed as will draw out the photographic analysis to a maximum visible extension. These considerations point to the superiority of a few cm. of flame-path near the spark, as a basis of comparison of results. This gives the further advantage, that the photograph of the spark itself is generally extremely well defined and therefore is a convenient point from which to measure.

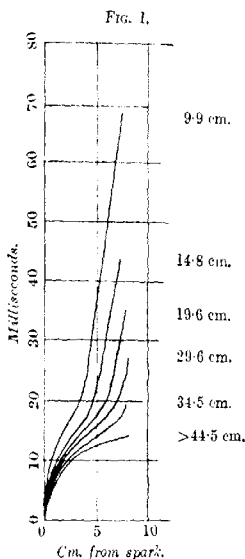
In all the results where the flame-path considered is not expressly stated, calculations have been based on the average speed of the flame over the first 5 cm.

I. The Firing Cylinder.

i. The flame starts slowly from the spark with regularly increasing velocity. If we consider any given point in its path, the velocity at this point varies with the length of the "arm" of the tube, that is, with the distance of the spark from the closed end towards which the ignition is spreading. It increases as this distance

increases until a maximum rate is reached. After this, the velocity at our selected point is unaffected by further increases in the length of the arm of the tube; it is also unaffected by opening this closed end.

The lower half of Table I shows that in the circumstances of the experiments, if the length of the arm of the tube be 67.3 cm., the velocity of the flame is not modified, at any point within 2.5 cm. of the spark-gap, by closing the open tube. At some point between 2.5 cm. and 5 cm., however, the velocity begins to be markedly modified, the mean speed over 5 cm. being reduced from 4.71 to 4.45 metres per second. Thus for measurements based on 2.5 cm. of flame-path, there is a "minimum distance" from spark to closed end which is the equivalent of an open end. To base calculations on 5 cm. of flame-path requires, *ceteris paribus*, a greater "minimum distance"; but the "minimum distance" is also affected by other considerations: it is less the quicker the flame (Phot. 1.) and it is less the wider the tube (Table I). The tables demonstrate that as the arms of the tubes to the right of the spark were diminished, the speed of the flame-front travelling in that direction was decreased. The results lie on a smooth curve. The arm of the tube to the left of the spark-gap was of constant length.



In another series of experiments, the progress of the flame-front was traced from the film on to graph-paper. The trace of the flame on the film being a distance-speed curve with the spark at the origin, a number of these traces brought to a common origin yield the interesting comparison presented here as Fig. 1. The affixed numbers show the length in cm. of the progressively shortened arm of the tube along which the flame was travelling from the spark. Considerable assistance was received in these experiments from Mr. S. R. Stubbs.

ii. With central ignition, the propagation is symmetrical, diverging flame-fronts approaching opposite ends of the tube, each giving a

TABLE I.

Length in cm. of pro- gressively shortened arm.	Average speed in metres per sec.		Length in cm. of pro- gressively shortened arm.	Average speed in metres per sec.	
	Over first 5 cm.	Over first 2.5 cm.		Over first 5 cm.	Over first 2.5 cm.
Diameter of tube 20 mm.			Diameter of tube 13 mm.		
Open	3.96	2.61	Open	4.71	3.12
44.5	3.82	2.60	67.3	4.45	3.11
34.5	3.51	2.38	41.2	4.38	3.07
29.6	3.30	2.22	26.1	3.18	2.56
24.6	3.05	2.10	21.3	Phase I does not cover	2.25
19.6	2.78	1.93			
14.8	2.31	1.77			
9.9	Phase I does not cover	1.53	11.4	Phase I	1.57
	5 cm.		6.5	does not	0.77
			3.8	cover even	0.48
				2.5 cm.	

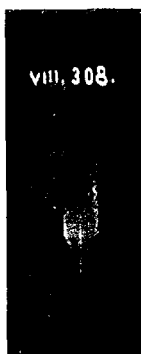
photographic analysis which is the mirror-image of that of the other. Asymmetry is obtained, however, even with central ignition, if the spark-gap does not mark an exact balance of volume as well as of length, or if there is any other circumstance making for asymmetrical resistance to the pressure caused by the progressive inflammation. Phot. 2 shows the result of central ignition in a tube (filled by a capillary at the middle) plugged—but not sealed—at each end. The brass end-plugs were inserted to an equal distance, but one fitted slightly more tightly than the other, and this asymmetry is reflected in the slight asymmetry of the photographic analysis. The arms of the tube were not long enough to produce visible symmetry even over a very small range near the spark-gap.

If ignition be not central, the flame-front approaching the nearer end will be slower than the other; and this is true of every point in the flame-path in reference to which the length of the arm of the tube is less than the "minimum distance." Phot. 3 shows no visible symmetry at all. This, as indicated above, is due to the fact that the shorter column of gas offers more resistance to the pressure caused by the combustion than does the longer one.

iii. The resistance offered to one flame-front must tend to help the progress of the other. An increase in speed on this account has been actually measured where the latter flame was extremely slow and was travelling along a very short arm of the tube. In some of the experiments referred to in Table I, photographs were taken of the flame in the short arm of constant length. Table II (in which a is the length of the progressively shortened arm of the tube to the right of the spark, and b is the average speed of flame over the first 2.5 cm. in the uncut arm to the left) shows how, as the tube was cut down, this assistance came to a maximum and then diminished as the actual combustion in the progressively



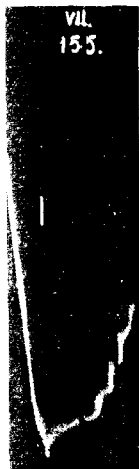
1.



2.



3.



4.

1. The upper flame is from a breakflash unit (2.6 "theoretical" carbon disulphide) at mixture in a 20 mm. tube, 83 cm. long, with the spark 73 cm. from one end. Reference marks at 5 and 10 cm. from the spark. The flame is arrested just within the field of the photograph. The wheel continued to run while the tube was again filled with the mixture and fired again, but with a spark from a condenser (0.000025 c.c. of air). The flame is faster and shows no sign of arrest within the field of the photograph.

2. The same mixture in a 20 mm. tube, with central ignition by a breakflash, the length reduced to a total of 5 cm. by the plates referred to in Section I, d.

3. The "theoretical" carbon disulphide-air mixture, fired at 2 atm. in a 14 mm. tube, 32.5 cm. long; spark gap 73 cm. from the end.

4. The "theoretical" carbon disulphide-air mixture, fired in a 10 mm. tube, 32.5 cm. long, the spark gap 73 cm. from the end.



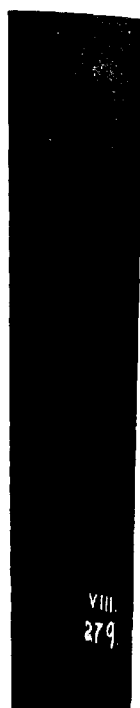
Vol.
124.



IX.
147.



VIII.
276.



VIII.
279.

shortened arm became very small. The results lie on a smooth curve.

TABLE II.

a.	Open	66.3	41.2	26.1	21.3	11.4	6.5	3.8	0.2 cm.
b.		1.80	1.86	1.91	2.37	2.34	2.29	2.10	1.73 1.40 metres per sec.

iv. Up to this point, we have considered merely the initial phase—that characterised by regular acceleration. In an air-tight, closed tube, however, this phase does not continue along the whole length of the arm of the tube. In his paper "On the Movements of the Flame in the Explosion of Gases," Dixon (*loc. cit.*) has shown that, in high-speed detonating mixtures, this phase commonly ends when a sound-wave, starting at the firing-point and reflected from the end of the tube, meets the advancing flame-front. The greater part of the present research, however, has been concerned with very slow mixtures, and Mason and Wheeler (T., 1920, 117, 38) have already demonstrated that slow mixtures exhibit the sequence

"Uniform movement,"

Vibratory period of constant mean value,

Vibratory period, mean speed decreasing,

—when fired from the open end of a tube—in place of the sequence; described by Mallard and Le Chatelier,

"Uniform movement,"

Vibratory period,

Detonation,

which is exhibited by high-speed detonating mixtures.

In our experiments, the flame-front enters upon a second phase, Phase II, of slow and almost perfectly constant speed (Phot. 3), which can be easily followed by the eye and lasts until the flame reaches the end of the tube. (If the distal end of the tube be open, this second phase will be characterised by slow oscillations and will, in this case, probably be identical with the final phase of the "Uniform movement" sequence. In large-bored tubes, Phase I merges into Phase II with a smooth bend in the photographic analysis. As the bore decreases, this bend becomes a sharp turn, and with the smallest bores, especially with end ignition, Phase II is ushered in by a few oscillations (Phot. 4). If the mixture be a fairly fast one, oscillations will begin as soon as Phase I ends and will continue, but with no regularity of amplitude, until the flame-front reaches the end of the tube, each oscillation throwing back a pressure-wave through the burning zone. Of the inception of this second phase, it may be remarked:

A. That it does not occur in the circumstances of Plot. 2, that

is (a) it is dependent on the pressure in the flame and beyond it, (b) it is not, in slow mixtures, impulsive.

B. That it begins when the zone ignited during Phase I has passed its maximum luminosity, and almost simultaneously in both flame-fronts (Phot. 3).

C. That the zone ignited during Phase I is contracted as Phase II begins and proceeds (Phot. 5).

D. That as Phase II continues, the flame-front grows brighter in front; behind, it extends toward the central zone (Phot. 3).

E. That there is a comparatively dark zone between this flame and the central, contracting zone. This causes the latter to be frequently well-marked in the photographic analysis.

F. That when mixtures are fired at high initial pressure and a subsequent spark is passed in this dark zone, the photographic analysis shows the track of a luminous motion which begins at the spark and is nearly uniform in speed in its slow journey toward the central, contracting zone (Phot. 6). A similar phenomenon, which has been termed a "flame-cap" or "aureole" (Burgess and Wheeler, T., 1911, 99, 2013; 1914, 105, 2594), is known to occur when a *current* of a mixture below the dilution limit of inflammability passes over a source of ignition.

G. Phase II begins nearer the spark-gap in circumstances associated with quicker cooling, namely, with a slower flame (Phot. 1) or in a smaller bored tube (Bone, Drugman, and Andrew, T., 1906, 89, 1614).

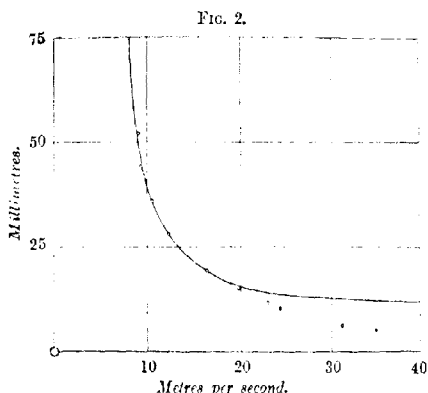
These points may all be explained by supposing—as seems reasonable, that the movement of flame in these slow mixtures is actually modified by mass movements of gas in the tube. The pressure of the unburnt column of gas must continue to increase with the pressure in the flame; when the flame-pressure begins to fall, the uncombined compressed gas will tend to push the flame backward. Is it not probable that Phase II begins at the moment when the outward surge of pressure, due to the ignition, is reversed by a backward stream?

v. In mixtures capable of detonation, the arrival of the flame at the end of the tube may be signalised by a very fast pressure-wave, registered on a slowly moving film as an almost horizontal line or band. In such mixtures, if one arm of the tube be long or open, the flame, in its initial phase, may be overtaken by a wave from the end of the tube behind it. The speed of the flame-front is then greatly increased. This is one of the principal reasons why the period between ignition and the setting up of the detonation wave has been found to vary with the distance of the spark-gap from the firing end (Dixon, *loc. cit.*, p. 345).

vi. The various movements which have been described are all slower with wider bore of tube, where this is the only variable. It may be predicted that the period between ignition and the setting up of the detonation wave, when the charge is fired near a closed end, will be greater, within limits, the wider the bore. A typical bore-speed curve is shown in Fig. 2. It is that of the "theoretical" ethylene-air mixture. The points only are indicated. The curve drawn for reference, is that of the rectangular hyperbola

$$(x - 6.58)(y - 8.1) = 109.2.$$

Between bores of 52 mm. and 15 mm., the results follow this curve very closely. Below 15 mm., the viscosity of the walls of the tube



and the great increase in the "cooling factor" effect a slowness of increase in speed, in place of the immense increases required by the hyperbola. It is not impossible that an inflexion of the curve for some bore less than 5 mm. might be found: that is, one might arrive at a bore so small as almost, but not quite, to strangle the progress of the flame. The speeds were measured over the first 5 cm. from the spark. It was found that the "minimum distance" of tube-end from spark-gap, which would not affect the speed over the first 5 cm. of flame-path in the narrower tubes, was much greater than had been provided for, the set of tubes being all of the same length, and differing indeed in no particular save that of diameter. The curves first obtained thus showed an inflexion due to the confusion of two phenomena. This confusion was finally avoided by leaving the ends of the tubes open at the moment of firing.

vii. In imitation of the experiments of Campbell (T., 1922, **121**, 2483), it was found that if the flame, either in its initial or in its second phase, be led through a normal junction into a wider tube, co-axial with the first, the speed of the flame will be temporarily retarded.

II. Turbulence.

The effect of turbulence has been investigated by Schlösing and Demondésir (*Ann. Mines*, 1883, [viii], **4**, 298; also Ste.-Claire Deville's "Leçon sur la dissociation," p. 46), Hopkinson (*Proc. Roy. Soc.*, 1906, [A], **77**, 410; *Rep. Brit. Assoc.*, 1912, 203), Clerk (*Rep. Brit. Assoc.*, 1912, 201), and Wheeler (T., 1914, **105**, 2595; 1919, **115**, 83; 1920, **117**, 1227). It was hoped in the present work to gain some information as to the manner of the undoubted increase in speed and the apportionment of the increase between the two phases of the progress of the flame-front.

The charges used were the "theoretical" air-mixtures of the fuels indicated in the table. The variation in type of spark, due to the inability of our break-flash to ignite the pentane mixture, produced this interesting result—that the increase in speed due to turbulence is greater, *ceteris paribus*, for a weak spark. This would be a fresh proof, if need were, of the mechanical effect of the spark (Coward, Cooper, and Jacobs, T., 1914, **105**, 1069). This greater increase is naturally effected during Phase I, Phase II not showing as great an increase as for a spark of greater energy.

In general, Phase I shows an increase in speed due to turbulence of about 10 per cent.: Phase II, a much greater increase. The exception is the acetylene mixture, which is the fastest of all and shows least change in speed, due to turbulence, over the whole path. This exception is in agreement with the statement of Wheeler (*loc. cit.*) "that a mixture in which the speed of flame normally is slow should be more susceptible to the effects of turbulence than one in which the speed of flame normally is rapid."

The photographs obtained in this series of experiments indicated roughly to what extent the period of combustion was shortened by the turbulence, although the end of the luminous period is not recorded with any precision.

It should perhaps be stated that the arrangement of the apparatus and the relative distances of the various parts were kept rigidly constant, having been measured and noted at the outset of the experiments. The results are set out in Table III.

III. The Spark.

The effect of variable spark-intensity on the speed of the flame has been noted by Berthelot (*Compt. rend.*, 1882, **95**, 199), Parker

TABLE III.

Fuel.	Spark.	Condition.	Time over 1st 5 cm. (Roughly Phase I.)	Time over 2nd 5 cm. (Roughly Phase II.)	Total time over 10 cm.	Duration of effective luminosity.
			Milliseconds.			
C ₄ H ₁₂	Ordinary compound induction spark	Quiescent	13.2	13.0	26.2	76.3
		Turbulent	11.4	7.8	19.2	56.3
		% decrease	13.8	40.0	26.9	26.2
C ₂ H ₄	"	Quiescent	7.63	8.72	16.35	No record
		Turbulent	6.35	6.17	12.52	
		% decrease	16.7	29.8	23.4	
C ₂ H ₂	Condenser spark	Quiescent	7.42	7.26	14.68	105.2
		Turbulent	6.64	6.64	13.28	76.3
		% decrease	10.5	8.6	9.55	36.3
C ₆ H ₁₄	"	Quiescent	17.2	21.15	38.35	74.2
		Turbulent	15.7	12.62	28.32	69.7
		% decrease	8.75	40.4	26.2	6
CS ₂	"	Quiescent	10.41	15.58	26.0	91.5
		Turbulent	9.62	8.55	18.27	78.8
		% decrease	7.7	45.3	30.2	13.9
CS ₂	Break- flash	Quiescent	12.79	16.72	29.51	95.5
		Turbulent	10.92	16.50	27.42	73.2
		% decrease	14.4	37.2	27.4	22.3

(T., 1915, 107, 337), and more particularly by Wheeler (T., 1917, 111, 1056), who has illustrated it in some detail in experiments on ethane-air mixtures (T., 1911, 99, 2029).

The two most convenient ways of effecting an increase in spark-energy were

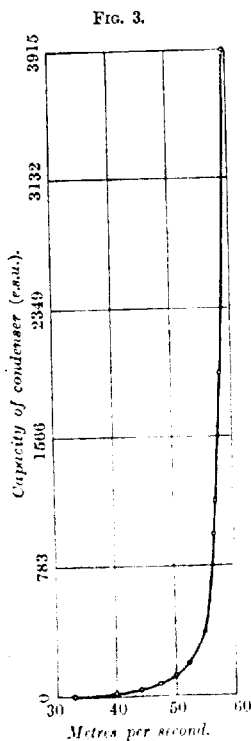
(a) to increase the capacity in the spark-circuit by connecting a variable condenser in parallel.

(b) to increase the width of the spark-gap, using a wide-bored explosion-tube with lateral capillary arms, through which the platinum electrodes, soldered to copper wires, were introduced, the gap being measured on a strip of stiffened, calibrated graph-paper.

(a) In the first series (Fig. 3), the use of a long narrow tube avoided unnecessary dissipation of the great mechanical energy of the spark (Coward, Cooper, and Jacobs, *loc. cit.*). In these circumstances, however, it was only possible to measure the initial phase.

The speed of the flame, measured over the first 4 cm. of its path, increased quickly with the capacity until the latter reached 0.000435 microfarad (or 392 e.s.u.); it then increased very slowly and uniformly till, when the capacity reached 0.00217 microfarad, it appeared to be nearly constant. The luminosity, however, increased up to the maximum capacity, 0.00435 microfarad, of the plate condenser, which was specially made for this work by Mr. Nathaniel Walker, who also assisted in the experiments.

(b) In the second series, in which considerable assistance was rendered by Mr. Henry Robinson and Mr. S. R. Stubbs, the unavoidably great width of tube was responsible for a smallness of increase in speed, our maximum increase being only 38.5 per cent. The spark was passed by momentarily "making" a mercury connexion in the primary circuit of an induction coil capable of a



5-inch air-spark. The current was furnished by four 2.1-volt accumulators in series. In order to avoid premature weak ignition from brush-discharges, the mixture used was the "theoretical" pentane-air mixture which, we found, could not be ignited by a "make" or "break"-flash from our circuit. The trembler of the induction-coil was adjusted therefore to give the compound spark, containing a "capacity component."

The results seem to show that the speed increases with the spark-gap almost rectilinearly up to a certain point which depends chiefly on the strength of the current in the primary circuit and the winding ratio of the induction coil.

In the figures given (Table IV), the straight-line relation ends when the spark-gap is in the neighbourhood of 20 mm., after which the increasing tenuity of the spark is probably responsible for an inflexion in the curve.

The slower flame-front was not difficult to measure. The faster one, however, was often found to be travelling obliquely, the photographic analysis showing a double edge. In such cases, the mean was taken. One photographic analysis showed a triple edge, registering apparently an oblique flame-front which was also cup-shaped.

IV. Temperature.

Mallard and Le Chatelier (*Ann. Mines*, 1883, [viii], 4, 348) predicted and proved that the influence of increased initial temperature was to increase the speed of propagation of the "uniform movement" of flame through a mixture. There was every reason to

TABLE IV.

Width of spark- gap in mm.	Mean speed of slower flame-	Mean speed of faster flame-	Width of spark- gap in mm.	Mean speed of slower flame-	Mean speed of faster flame-
	front over the first 5 cm.	front over the first 5 cm.		front over the first 5 cm.	front over the first 5 cm.
	Metres per sec.	Metres per sec.		Metres per sec.	Metres per sec.
1	3.13	4.30	20	3.55	5.57
3	3.20	4.45	28	3.65	5.82
5	3.25	4.60	38.5	3.60	5.95
9	3.35	4.95	51	3.50	5.85
14	3.47	5.25			

suppose that the same would be true of this kind of propagation. Woodbury, Lewis, and Canby (*J. Soc. Automotive Engineers*, 1921, 8, 209), however, firing acetylene-air mixtures at the base of a vertical cylinder, 4" \times 12", obtained results which "indicated that increased temperature produced little effect upon the rate of flame propagation."

Now a quantitative study of the effect of variation of the initial temperature cannot usefully be carried out without a parallel determination of the extent to which pre-flame combustion, or "baking," has proceeded during the time during which the charge has been subjected to the heating agency.

The present determination was purely qualitative. Various heating arrangements were tried. The first gave results which indicated either that change of initial temperature produced no difference in speed, or that the loss of speed consequent on dilution due to baking balanced the gain in speed due to the rise in temperature. The second took so long to raise the mixture to the desired temperature that when the spark was passed the mixture refused to ignite—an informing comment on the first experiments. The third method, suggested by Mr. Henry Robinson, heated the mixture so quickly and uniformly that it was possible to repeat and corroborate the result.

In the case of the hot mixture, as will be seen by the comparative photographs (7, i and ii), the initial phase is faster and the flame less luminous. Moreover, the initial phase ends nearer the spark, thus providing a suggestive exception to the generalisation in Part I., iv., G., that Phase II begins nearer the spark-gap with a slower flame.

TABLE V.

Temperature.	Time to travel 5 cm. from spark.	Time occupied by Phase I.
	Milliseconds.	Milliseconds.
16.4°	13.17	18.02
16.6	12.82	18.3
86 approx.	10.27	13.57
96 approx.	9.76	13.22

V. Pressure.

Woodbury, Lewis, and Canby (*loc. cit.*) state that "The results obtained on various mixtures of acetylene and air, under initial pressures of from one to four atmospheres, indicated that with each gas mixture, the rate of propagation increases with an increase in the initial pressure up to a critical density and that with any further increase in the pressure above that critical value, no increase in the rate of propagation is obtained."

FIG. 4.

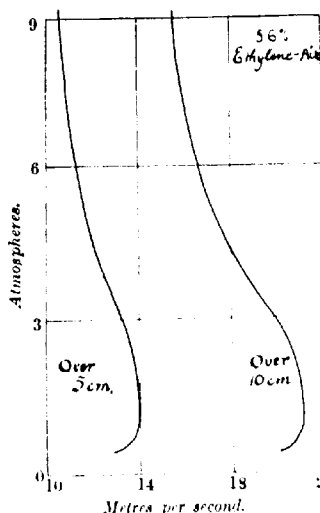
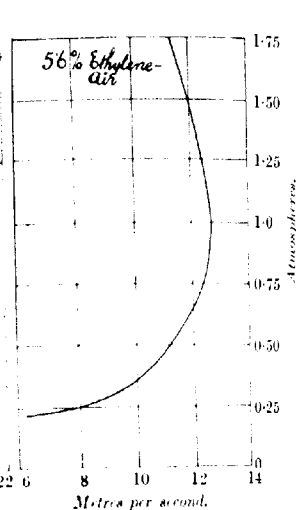


FIG. 5.



The results of the present investigation differ from these in important particulars. In all the many mixtures which have been subjected to experiment, the pressure for maximum speed has proved to be one atmosphere. Below this pressure, the speed has declined gradually to about half an atmosphere, and then quickly, but smoothly, to the limiting pressure. Above atmospheric pressure, the speed has decreased continuously with the increases of pressure. Mixtures have been fired at 15 atmospheres pressure (Phot. 5), one of the most surprising features of this work having been the very great initial pressure which glass tubes will stand without rupture. Numerous experiments have been carried out with an initial pressure of 9 atmospheres without injury to a tube of 21 mm. diameter; and on one occasion, with a weak spark—the

condenser having been disconnected—a mixture was fired at 15 atmospheres in a tube of 13 mm. diameter without breaking it.

The decline in speed above 6 atmospheres is, however, very small; the curve appears to approach an asymptote. Below this pressure, it seems to vary, in exact detail of shape, with the fuel content of the mixture. There is no sign of a critical pressure except the inflexion at one atmosphere, and a slow bend of the curve at a higher pressure which varies with fuel content.

FIG. 6.

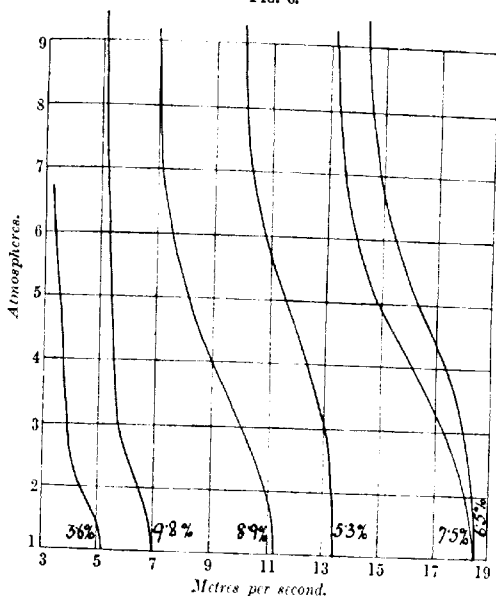


Fig. 4 shows a typical curve for a 5 cm. flame-path, with the corresponding curve for 10 cm. of flame-path by its side. The tube was not injured in any way by these and other experiments with air-mixtures at these pressures. The thickness of the wall of the tube was 2.7 mm.

Fig. 5 is a detailed study of the region near atmospheric pressure.

Fig. 6 shows a series of ethylene-air mixtures in a tube made to the same measurements as that used for the experiments of Fig. 4. The slow bend in the curves, which has already been noted, seems to mark some kind of progression from limit-mixtures to the maximum-speed mixture.

These are all ethylene curves; but the fuels used have included methane, carbon disulphide, pentane, benzene, ethyl alcohol, hexane, ether, and acetylene.

There is a marked parallelism between the temperature and pressure results of this investigation and those of Terres and Plenz (*Chem. Centr.*, 1915, ii, 1278) and Mason and Wheeler (*T.*, 1918, 113, 53) on the effect of variation of initial conditions on the dilution limits of inflammability. In both cases, the pressure results are difficult to explain. It is possible that the results of the present work are accounted for by the facts which Mason and Wheeler tentatively advance as a possible explanation of theirs. They write: "According to the kinetic theory, loss of heat from gases by conduction and radiation is independent of the pressure. When attempting to put this deduction from the kinetic theory to experimental proof, however, Kundt and Warburg (*J. Physique*, 1876, 5, 118) found that unless the pressure of the gas was low, the loss of heat due to conduction was masked by that arising from convection currents. It may be, therefore, as Terres and Plenz have suggested, that the loss of heat from a gas at high pressure is due to a greater extent to convection than to conduction, and increases with the pressure."

In Section I, iv, F, of this paper, a phenomenon was noted which would imply that when a mixture is fired under great initial pressure, a mass of gas through which the flame has already passed becomes reignited, to a small extent, by a subsequent spark. This supposed flame-cap (Phot. 6), which appears to travel in a gentle current toward the middle of the tube, has been noted when the initial pressure was respectively 3.9, 5.1, 5.35, 6.25, 6.8, 7.0, and 7.7 atmospheres, but never when the initial pressure was atmospheric. Is it possible that, under pressure, these flame-caps are formed when the proportion of fuel is very low? In this case, that is, if increase of pressure actually extends the lower limit of the range in which flame-caps can be formed, such an extension is in strange contrast to the constriction of the limits of inflammability, where we find the lower limit raised. At the same time, it cannot be argued that increased pressure should tend in every respect to inhibit combustion, for Mason and Wheeler (*loc. cit.*) find, for instance, that it renders a mixture more easily ignitable by a weak spark.

The alternative conclusion (implicit in the theory of Frankland [*Phil. Trans.*, 1861, 151, 653. Experimental Researches, p. 901], that the completest combustion takes place in partial vacua) would be that the proportion of gas left unburnt on the supposed local extinction of the flame is so great, under high pressures, as to be only just below the dilution-limit of inflammability.

Neither alternative appears to be immediately susceptible of absolute proof or disproof. This applies also to the hypothesis of the formation of molecular aggregates at higher pressures, a theory by which Barss (*Amer. J. Sci.*, 1912, [iv], **34**, 229) explained certain phenomena due to change of pressure in his researches on ionisation by collision. This convenient theory would certainly account for

- i. the slower spread of the flame through the mixture;
- ii. the fact that in some very rich mixtures, luminosity actually decreases with increase of pressure;
- iii. the inefficient combustion effected during the first spread of the flame.

That the maximum-speed pressure should be one atmosphere is also a somewhat surprising result, the explosion system being nearly isolated from all gains and losses of heat except those due to radiation. The differences in this region are, of course, very near the experimental error. In order to get greater variation, a bigger tube was used, and a greater speed of film-wheel. This change of tube contributed two advantages: a slower flame and a greater luminosity. The slowness was further exaggerated by moving the position of the spark-gap to a point nearer the distal end.

In a tube 32.5 cm. long, of diameter 53 mm., the spark gap being 7.5 cm. from the end, a 5 per cent. mixture of ethylene-air gave—referring to 5 cm. of flame-path—photographic extensions measuring 76 mm. and 73.5 mm., respectively, for pressures of 1 atmosphere and 0.812 atmosphere. This difference of 2.5 mm., which would have been slightly greater had the film been travelling exactly the same rate in each case, is well outside experimental error. The speeds were

1 atm.	5.94 metres per sec.
0.812 „	5.63 „ „ „

Unfortunately, this tube was broken. With a similar tube of 43 mm. bore, the film-rate in the two experiments being the same, the results for pressures of 1.0 and 1.2 atmospheres, respectively, were photographic extensions of 54.5 mm. and 58.3 mm., or speeds of 7.23 and 6.77 metres per sec. The maximum for this mixture evidently lies between 0.8 and 1.2 atmospheres.

For the brighter 6.5 per cent. ethylene-air mixture, the maximum range was narrowed down to 0.9–1.1 atmospheres. The photographic extensions varied from 44 to 46.2 mm. The speeds were

0.9 atm.....	8.79 m.p.s.	1.1 atm.....	8.76 m.p.s.
1.0 „	8.95 „	1.2 „	8.58 „

Under similar conditions, the 6.53 per cent. carbon disulphide-air mixture gave

0.9 atm., 5.12 m.p.s.; 1.0 atm., 5.32 m.p.s.; 1.1 atm., 5.11 m.p.s.

Assistance in this work from Messrs. Henry Robinson, S. R. Stubbs, and F. W. Higgins is thankfully acknowledged.

EXPERIMENTAL.

Mixtures involving the use of liquid fuels were made by bubbling the measured dry gases composing the "atmosphere" through the liquid, which had been run into a small wash-bottle from a fine calibrated burette. More recently, the liquid has been measured gravimetrically and the volume of the "atmosphere" gases adjusted in exact proportion.

The long delivery tube of the glass "carburettor" ended in a glass 3-way tap, which on one side led upward through a cylindrical joint of litharge-and-glycerine cement to a flexible, asbestos-lined bronze tube. This led to one of a pair of mercury gas-holders, which were connected together by a similar tube. The mixture was quickly brought to homogeneity by passing it backward and forward between the two gas-holders. From the gas-holders, the first-mentioned bronze tube led the mixture back, via the three-way tap also mentioned, to a compact range of three glass 3-way taps. The first of these was a connexion through yet another flexible tube and union-joint to a brass tap and sheath with adjuster collars, which was used to carry explosion-tubes when it was necessary to use long or open tubes, or to have them very near the camera. The second of the 3-way taps connected the apparatus with the manometer and pump; this connexion was provided with a side-tube which permitted suction to be used for raising the mercury level in the right drum. The third 3-way tap was an emergency connexion with a Buchner filter-flask, for the evacuation of mercury from the apparatus in case of any flooding due to leaks.

The end of the range of taps was fused to a glass tube which was cemented into an iron three-way, so that the gas-mixture could be passed either through a needle-valve into the explosion-tube, held in the clamped frame, or down into a 5½-litre steel drum, connected at the base with an auxiliary drum, the latter communicating at the top with a safety-valve and a cylinder of compressed air. These drums were only used in the experiments on high pressure. In this work, the explosion-tube was, as usual, filled by evacuation to 2 cm. pressure, followed by filling and flushing with a large amount of mixture; but it was more convenient to fill the left drum with the mixture by first filling it with mercury, and then—the rest of the system meanwhile having been filled with mixture and opened

to the drum—to run the mercury out through a tap at the bottom, or transfer it by suction into the auxiliary drum. Mixture from the gasholder thus followed the mercury level, and the end of this operation left both the explosion-tube and the left drum full of the mixture. The drums were now shut off from all the rest of the system except the explosion-tube and the gauge carried by the iron three-way, and the compressed air was turned on until the desired pressure was registered on the gauge. The explosion-tube was then shut off from the rest of the apparatus, and fired. The frame holding the firing-tube consisted of two horizontal guides and two flat vertical end-pieces, fitted with needle-valves. The rose-jet introducing the mixture was shaped at the centre to receive the end of a rotating spindle (in the experiments on turbulence) or a thermometer (in those on temperature). The ground edges of the tube were protected by rubber washers; and the wing-nuts on the threaded ends of the horizontal guides were tightened until the system supported a vacuum. When a tube of only small diameter was used in conjunction with the frame, the outer end was held in position by a brass end-plug, the annulus of which provided a seat for the rubber washer. It was supported by a small bayonet, working on a stout spring at the centre of a brass casting which moved on the horizontal guides at their free ends, and was secured by the wing-nuts on their threads. For experiments at very high pressures, the end-plug was covered by a small length of brass tubing, so that the end of the glass tube abutted on the rubber base of a hollow brass annular prism.

In the turbulence experiments, a glass chimney, half the length of the cylinder, was supported coaxially within it by three pieces of asbestos rope. The spindle, lying in the axis of the tube, carried vanes which were rotated inside the chimney by a straight drive which communicated the speed of a motor through an air-tight gland. A V-shaped pair of electrodes provided a spark-gap which "cleared" the spindle. On one side of this central firing-point, the tube was quite clear save for the spindle; and it is the flame-front in this half of the tube that was studied. The vanes were rotated so that any mere current effect would diminish the speed of the flame.

In the temperature experiments, the thermometer lay in the axis of the tube, which was surrounded by a canister with highly polished interior. Outside, the canister had been carefully covered by pieces of asbestos board. Inside, and on the base of the canister, was an electric resistance heater. The tube was evacuated to 2 cm. pressure; and when a suitable temperature was indicated by the thermometer, read through a glass window in the canister, it was

filled and then flushed with the charge-mixture. The filling was carried out in stages, to guard against the effects of a spontaneous ignition.

After a measured interval, the thermometer was read again, and the ignition of the mixture was then photographed through another window in the canister.

Other experimental details may be summarised as follows:

Reference.	Length of tube.	Constant distance of spark-gap from end (cm.).	Type of spark.	Bore of tube.	Mixture.
Table I	Shown	12.6	Condenser Cap. 0.000435 mf.	Shown	CS ₂ + 3O ₂ + 17N ₂
Fig. 1	"	7.1	"	20 mm.	"
Table II	"	12.6	"	13 mm.	"
Fig. 2	32.5 cm.	7.3	Cap. 0.000652 mf.	Shown	Ethylene + theo. air
Table III	33.5 cm.	18.75 (Central)	Shown	51 mm.	Shown
Fig. 3	83.0 cm.	6.1	"	13 mm.	C ₂ H ₄ + 3O ₂ + 7N ₂
Table IV	32.5 cm.	10.0	Described	52 mm.	Pentane + theo. air
Table V	32.5 cm.	7.3	Break-flash	52 mm.	CS ₂ + theo. air
Fig. 4	35.5 cm.	2.9	Condenser Cap. 0.000435 mf.	21 mm.	Shown
Fig. 5	35.5 cm.	0	"	27.5 mm.	"
Fig. 6	35.5 cm.	2.9	"	21 mm.	"

The spark-gap was uniformly 1 mm., except in the experiments referred to in Table IV.

The author is indebted to Mr. J. Bamber of the Engineering Department for many most valuable suggestions in the construction of the heavier apparatus, which was made by him.

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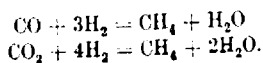
[Received, March 26th, 1923.]

CLXIX.—Promotion of Catalytic Reactions. Part I.

By SAMUEL MEDSFORTH.

A. The Action of Hydrogen upon the Oxides of Carbon.

IN the course of experimentation on the oxidation of methane, it became necessary to prepare large quantities of this gas, and for this purpose various methods of preparation were studied, including the well-known Sabatier reactions:



The quantities of the reacting gases in the case of carbon monoxide were those used in the Cedford process for the production of methane (*J. Gasbeleucht.*, 1911, **54**, 737), that is, one part of carbon monoxide to five parts of hydrogen. The catalyst was nickel prepared *in situ* by the reduction of the oxide from nickel nitrate deposited on pumice.

In considering the above equations, it will be observed that water is one of the end-products, and it was thought that the presence of a catalytic dehydrating agent in contact with the nickel catalyst would materially increase the velocity of the reaction. The results of preliminary experiments were sufficiently interesting to warrant further investigation.

The effectiveness of promoters in catalytic reactions is now a well-established fact; the Badische Company state that the oxides of thorium, glucinum, and zirconium are capable of functioning as promoters in the methane synthesis (D.R.P. 2306, 1914).

Pease and Taylor (*J. Physical Chem.*, 1920, **24**, 241) define promoter action as including "all those cases in which a mixture of two or more substances is capable of producing a greater catalytic effect than can be accounted for on the supposition that each substance in the mixture acts independently and in proportion to the amount present." The maximum accelerative effect will be obtained when the number of points of contact of the promoter and catalyst exposed to the reacting substance or substances is at a maximum. On this view, therefore, it should be possible to determine the optimum catalytic effect on the velocity of a reaction by means of a series of experiments in which the proportion of promoter to the same quantity of catalyst is varied. This optimum concentration will differ with each substance and with the method of preparation. It is difficult, if not impossible, to secure uniformity of deposition of the catalyst and promoter on the surface of the carrier, and therefore too concordant results were not be expected. It was found that in addition to the surface effects, the temperature at which the catalytic effect was at a maximum differed with the substance used, having regard of course to the production of undesirable by-products. The results shown in this paper are in the majority of cases the mean of a number of determinations.

Table I shows in column I the maximum catalytic effect produced by the use of the substances enumerated on the formation of methane from a mixture of carbon monoxide and hydrogen ($\text{CO}:\text{H}_2 = 1:5$ by volume), and in column II the maximum catalytic effect on the synthesis of methane from carbon dioxide and hydrogen ($\text{CO}_2:\text{H}_2 = 1:6$ by volume). The figures refer in every case to the optimum concentration of promoter added to

the nickel, the quantity of which was kept constant throughout the experiments. The effect produced by nickel alone is taken as unity. The details of these experiments will be found in a later part of the paper. Columns III and IV show the increase in effect produced, taking that due to the promoter thorium as 100.

TABLE I.

Name.	Maximum effect.		Increase in catalytic effect.		Rideal and Taylor, Dehydrating properties.	
	I (CO ₂ H ₂).	II (CO ₂ H ₂).	III (CO ₂ H ₂).	IV (CO ₂ H ₂).	V.	VI.
Cerium oxide.....	17.7	Not det.	103.6			
Thorium	17.1	12.8	100.0	100.0	100	D
Glucinum	16.6	12.65	96.9	98.0	45.0	M
Chromium	15.7	11.40	91.4	88.2	91.0	M
Aluminium	14.3	10.45	82.6	80.1	98.5	D
Silica	12.3		70.2		84.0	M
Zirconia	8.9		49.1		45.0	M
Molybdenum oxide	6.3	2.2	32.9	40.1	23.0	M
Vanadium	4.0	1.35	18.6	3.0	9.0	M
Tin	No acceleration		0	0	0	
Magnesium	"		0	0	0	H
Copper	"		0	0	0	H
Silver	"		0	0	0	H
Nickel	1.0	1.0				

D = dehydrating agent; M = mixed dehydrating and dehydrogenating agent; H = hydrogenating agent only.

It was stated at the outset that the experiments were undertaken to discover the effect of the addition of a dehydrating agent to the catalyst on the velocity of the reactions given above. It is difficult to find a basis of comparison between the substances tested and the well-known catalytic dehydrating agents of a suitable type, for obviously the action of the latter will vary with each reaction investigated. Rideal and Taylor ("Catalysis in Theory and Practice," p. 288) give a list of oxides arranged in order of their dehydrating action on ethyl alcohol at 340–350°, counting the effect due to thorium as 100, and this table (column V) has been used for a first comparison. It will be seen from the table that with the striking exception of glucinum oxide there is a very fair measure of agreement between columns III and IV on the one hand and column V on the other, at all events in the general order of the oxides and metals. It can be stated therefore that the velocity of the reactions investigated can be increased by the addition of a small quantity of a suitable dehydrating agent to the nickel.

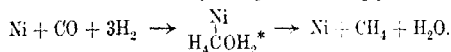
Theoretical Discussion on the Action of Promoters in the Methane Synthesis.

The study of promoters has received comparatively little attention and only a few suggestions are to be found on the possible mechanism

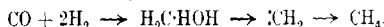
of their action. Catalysis itself has been regarded as a purely physical phenomenon, or as a purely chemical one, or as a combination of both. Surface conditions and surface action are of primary importance in catalytic work, but it was realised that considerations of physical phenomena (such as adsorption) alone would scarcely be sufficient to explain the precise mechanism of the reactions studied. It is not proposed therefore to discuss in this paper the physical aspects of the subject, but to indicate the probable nature of the chemical action of the various substances used as promoters.

(a) *Carbon Monoxide and Hydrogen*.—The formation of methane by the passage of a mixture of carbon monoxide and hydrogen over nickel may be explained in two ways:

1. The oxygen of the monoxide is considered to be quadrivalent and there is formed an unstable intermediate compound by the union of three molecules of hydrogen with one molecule of the monoxide, probably in combination with the catalyst (compare Sabatier and Senderens, *Ann. Chim. Phys.*, 1905, [viii], 4, 467). The course of the reaction may be represented simply as follows:

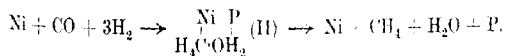


2. An intermediate compound of the methyl alcohol type is formed (probably *via* formaldehyde), which is dehydrated to give the residue $\cdot\text{CH}_2$ and water, the former being immediately hydrogenated to methane (compare Bone and Davies, *T.*, 1914, 105, 1694):



In both cases, the nickel is considered to be acting as a hydrogenating catalyst and as a dehydrating agent, and its power of functioning as the latter is known to be small. Consequently, the rate of formation of methane will be comparatively low. The presence, therefore, of a suitable dehydrating agent, even in minute quantity, at the surface of the nickel will increase the velocity of the dehydration and by so doing will leave the catalyst free to do the work of hydrogenation at an enhanced rate. In other words, the function of a promoter is to relieve the catalyst of part of its work, in fact to take over work which it can do better than the catalyst itself.

With nickel and a promoter, P, present, the reaction according to the first suggested mechanism may be represented as follows:

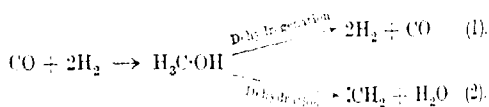


This formula represents the "complex" supposed to be formed after the intramolecular change has taken place.

According to this scheme, a double "complex" formation is assumed in which the promoter P combines loosely with the intermediate compound, formed by the union of the reacting gases with the catalyst. The nature of the promoter, that is, its dehydrating properties, indicate that it is attached to the remainder of the double "complex" as shown in II, that is, through the HOH group.

On this hypothesis, the activity of substances such as ceria, thoria, etc., and the inertness of others, for example, copper, silver, may be explained. The promoting power of a substance as far as these reactions are concerned becomes a function of its catalytic dehydrating effect on the intermediate compound supposed to be formed. Further, since the instability of the intermediate compound ensures rapid dehydration, a very high maximum catalytic effect is obtainable by the introduction of a powerful dehydrating agent, and Table I shows the extraordinary increase produced by such substances.

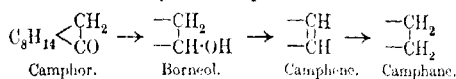
Now, in addition to the formation of methane another operation appears to take place when a mixture of carbon monoxide and hydrogen is passed over nickel. It has been shown by the author that if a mixture of one part of methyl alcohol and three of hydrogen (that is, the proportions in which these two substances would be present assuming the formation of the alcohol in the experiments described in this paper) be passed over nickel, the rate of decomposition of the alcohol into carbon monoxide and hydrogen will be far greater than that of the formation of methane. The rate of production of methane with thoria present is fourteen times that with nickel alone. These experiments would appear to show that when a mixture of carbon monoxide and hydrogen (1:5) is passed over nickel, rapid formation of an intermediate compound of the methyl alcohol type takes place (probably *via* formaldehyde) which is decomposable in two ways:



In addition, therefore, to acting as a hydrogenating and a dehydrating catalyst, the nickel functions also as a dehydrogenating agent, so that the promoter will, by increasing the rate of dehydrogenation, suppress the dehydrogenation and enable the nickel to hydrogenate at an enhanced rate.

Some experiments carried out by Ipatiev (*J. Russ. Phys. Chem.*

Soc., 1912, 44, 1695) seem to support the second view of the mechanism of the reaction and the dehydration hypothesis. He found that camphor was hydrogenated in the presence of nickel oxide at 320–350° to borneol. This in turn could be dehydrated at 350–360° in the presence of alumina to camphene, which could then be hydrogenated at 240° to camphane. By using a mixture of nickel oxide and alumina in the presence of hydrogen, camphor could be converted directly to isocamphane at 200° or less.



(See Pease and Taylor, *loc. cit.*).

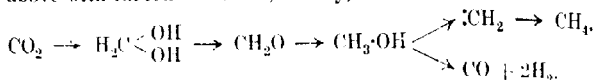
More information may be obtained on the mechanism of the reaction as a result of further experiments, particularly on the oxide of glucinum, as the cases in which this substance is more active than thoria or alumina are limited, generally, to the production of esters from mixtures of alcohols and acids (D.R.P. 261878).

Selective Promotion.—It will be shown in the experimental portion of this paper that in the presence of a promoter a slightly larger percentage of carbon dioxide is obtained in the final gas than with the catalyst alone, under conditions which preclude the possibility (verified by tests) of the decomposition of the carbon monoxide to the dioxide and carbon. Carbon monoxide will react with water as follows :



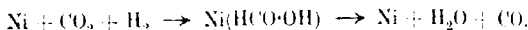
and, as is well known, promoters are capable of accelerating this reaction. The effect of various promoters has been determined and it is hoped to communicate the results in a later paper. It has been found that the velocity of this reaction at 180–280° is, with nickel alone, much smaller than that of the methane synthesis. It would appear, therefore, that when two reactions, both capable of being accelerated, take place at the same time in the presence of the same catalyst and promoter, that which is normally the slower is accelerated to a greater comparative degree than that which is normally the faster. Support for this statement was obtained whilst investigating the action of carbon monoxide on excess of steam in the presence of nickel, and nickel and promoters. Whilst carbon dioxide and hydrogen are the main products of the reaction, methane is also formed, the quantity of which is greater when, for example, alumina is present than when nickel alone is used. Selective promotion may be said to be operating in these two cases.

(b) *Carbon Dioxide and Hydrogen*.—The mechanism of this action may be expressed in a similar manner to that described above with carbon monoxide, namely,



This representation would explain the formation of carbon monoxide, which has been found in the exit gases by various workers, particularly where a large excess of hydrogen is not used.

Probably a simpler hydrogenation than that shown above (II) takes place, the result being a compound which is dehydrated to give the monoxide and water:



The production of methane from carbon dioxide and hydrogen appears therefore to involve two more operations than is the case with the monoxide. The catalyst takes part in an extra hydrogenation, and the promoter in a dehydration. This would account satisfactorily for the higher temperature necessary with carbon dioxide, and also for the somewhat lower accelerating effect obtained by the use of promoters.

Applications of the hypothesis outlined above will be considered after the experimental part (Section B).

EXPERIMENTAL.

Materials used.—(a) The carbon monoxide was prepared by the dehydration of formic acid with sulphuric acid and was freed from carbon dioxide by passage through a strong solution of caustic soda. The average purity throughout the experiments was 99.8 per cent. Cylinder carbon dioxide was used in the experiments involving this gas.

(b) The hydrogen was prepared electrolytically and was of a high order of purity (99.9 per cent.).

(c) The nickel used was prepared from nickel cubes (obtained by the Mond process) and contained a small proportion of iron and carbon. Comparative tests showed that these impurities were present in such small amounts as to have no influence on the results. A stock solution of nickel nitrate was made from the cubes, and finely divided nickel was obtained by the reduction of the oxide resulting from the ignition of the nitrate, deposited on pumice.

The temperature and time of reduction were varied according to the nature of the promoter, experience having shown that nickel

oxide after the addition of substances such as silica, capable of combining with it, required a higher temperature for reduction than did nickel alone or with promoters of the type of thorium oxide. In general, the reduction temperature was 330–350°,* rising to 450–470° in the case of nickel silicate.

(d) The substances tested for promoter action were obtained as pure as possible, but in many cases laborious purification was necessary before the results were trustworthy, chiefly owing to the presence of traces of poisonous sulphur-containing compounds. Thorium nitrate, for example, was purified both by recrystallisation and precipitation methods. In this work, with the exceptions hereafter stated, only irreducible or difficultly reducible oxides were used.

(e) *Pumice* (20–30 mesh), purified by boiling with concentrated hydrochloric acid, followed by the complete removal of the latter, was used as the support for the catalyst, after tests had shown that it was practically inert.

Preparation of Catalysts.—The preparation of the individual mixtures tested is noted below in Table II. Wherever possible, the following method was adopted. The pumice was added to about 10 c.c. of the mixed nitrates in solution in the desired proportions, and the mixture dried between 80° and 100° with stirring. The nitrates were then ignited at as low a temperature as possible until completely converted into the oxides.

It has been stated that precipitated alumina is much more active as a dehydrating agent than alumina prepared by the ignition of the nitrate. It was found actually that the method of preparation had only a slight influence on the activity of this substance in the methane synthesis.

Concentration of Catalyst.—In order to obtain comparative results, 1 gram of pumice was used in each experiment, and the amount of the nickel after reduction was 0.1 gram. The quantity of pumice taken was checked by measurement of the catalyst space in each experiment. The amount of promoter added varied over a wide range.

Temperature.—Carbon monoxide is decomposed more or less rapidly above 300° in the presence of nickel, and in the majority of the experiments involving this gas this temperature was not

* In view of the discussion as to the necessity of oxygen for the activation of hydrogenating catalysts (Willstätter and Waldschmidt-Leitz, *Ber.*, 1921, 53, [B], 113), it is of interest to note that whilst the lower oxides of nickel were themselves quite inactive in this synthesis, there is considerable evidence to show that they act as promoters to the nickel, which alone is only slightly active.

TABLE II.

Substance +nickel.	Optimum concentration as % of nickel.	Max. speed in c.c./min.	Temp.	Method of preparation.
Cerium oxide	4	620	270 ²	By ignition of nitrates,
Thorium	10—12	600	270	"
Glucinum	20	580	275	"
Chromium	15	550	295	"
Aluminium	15	500	297	"
Silica	7	430	295	By precipitation,
Zirconia	18	310	280	"
Molybdenum oxide ..	12	220	292	Ex. nickel nitrate, amm. molybdate,
Vanadium	7	140	298	Ex. nickel nitrate, amm. vanadate,
Tin	No acceleration			
Magnesium	"			
Copper	"			
Silver	"			
Nickel		32—35	285—290	By ignition of nitrate,

exceeded. It is to be noted, however, that the heat of reaction was sufficiently great to make temperature control a very difficult matter and the temperatures recorded below must be regarded as only approximately accurate.

Apparatus and Procedure.—The required mixture ($\text{CO} : \text{H}_2 = 1 : 5$ or $\text{CO}_2 : \text{H}_2 = 1 : 6$) was stored in an aspirator over gas-saturated, acidified water, from which it could be passed at varying speeds through a drying system and into the catalyst chamber. The latter consisted of a straight glass-tube, fused to a preheating coil disposed around it and heated in a carefully lagged air furnace, thermometers being placed both inside and outside the tube to indicate the temperature. After reduction was complete and before an experiment was commenced, the apparatus was swept out by a current of the mixed gases, and between separate experiments involving the use of the same catalyst, the latter was kept in an atmosphere of hydrogen. In addition to volume relationships, analyses of the exit gases were made and used as a further check on the accuracy of the aspirator readings.

Maximum Catalytic Effect.—In all cases, the catalytic effect of the substance under examination was measured by the maximum speed at which the gases could be passed over it, to ensure a complete or almost complete removal of the carbon monoxide or dioxide at the temperature employed. This was chosen as the most convenient point for comparison, although, of course, the space-time yield can be increased by reducing the time of contact of the gases with the catalyst within certain limits.

The optimum concentration was determined for a number of

promoters and the maximum speeds attainable at this concentration are shown in Table II. The speeds are compared with that obtained with nickel alone, that is, 32–35 c.c. per min. for 0.1 gram of catalyst on 1 gram of pumice at 285–290°. Great difficulty was experienced in estimating small alterations in speed with small changes in concentration of the promoter round and immediately beyond the optimum concentration. The figures representing the optimum concentration therefore are given to the nearest whole number and the higher speeds are accurate to about 10 c.c. per min.

In the above table those substances showing no acceleration* have been prepared by various methods and tested at different temperatures. All possible methods have not been exhausted, and it is proposed to continue experiments on these substances. The results obtained by the more detailed investigation of some of the promoters are shown in Table III.

TABLE III.

Quantity of promoter as % of Ni.	Maximum speed in c.c. min.						
	Ce ₂ O ₃	ThO ₂	GlO.	Al ₂ O ₃	Mn ₂ O ₃	V ₂ O ₅	Cu.
0.5	300	60	32	75	32	32	33
1.0	540	320	35	200	40	54	30
2.0	560	420	—	260	—	60	—
3.0	590						
4.0	620						
5.0	610	480	160	320	80	95	—
6.0						120	
7.0	660					140	
9.0		590				120	
10.0	600	600	290	450	200	110	26
12.0		600		470	220		
15.0	580	600		500	150		
16.0				400			
18.0			540				
20.0	560		580	460			
23.0			560				
50.0	470	570	420	380	110	24	No action
100.0		530	280				
200.0	380	470					
About 100		350					

The results tabulated above show that no relationship can be established between the molecular weight of a promoter and its optimum concentration. One per cent. of glucinum oxide, for example, with a molecular weight of 25, is one-ninth as effective as 1 per cent. of thorium oxide, with a molecular weight of 264, indicating that in the former case the nickel has covered the whole of the oxide, and in the latter the promoter has been deposited in part at the surface of the catalyst. With thoria and to a

* Sodium hydroxide, sodium carbonate, potassium carbonate have been shown to be ineffective as promoters in this reaction.

lesser extent with ceria, a large, ill-defined region exists in which quite considerable changes in concentration produce no corresponding effect on the velocity. In fact, above the optimum concentration there was not with the majority of promoters that decrease in velocity expected on the assumption that the increase in concentration diminished the surface of the catalyst exposed to the action of the gases. Surface conditions are evidently very complex at these concentrations, although it is probable that to some extent the decrease in surface of the nickel is counteracted by the increase in accelerating power of the promoter.

For these reasons, the curves in Fig. 1, showing the relationship between the concentration of the promoters named and the speeds, have not been continued far beyond the optimum concentration.

Surface Covered by Promoters.—It is desirable at this stage to attempt to form an estimate—necessarily only approximate—of the probable changes in exposed surface of the catalyst due to small differences in the concentration of the promoter, particularly round the optimum concentration.

Two cases will be considered, (1) in which both catalyst and promoter are deposited on a support, (2) the catalyst is deposited on the promoter.

1. With the amounts of nickel and pumice used above, that is, 0.1 gram of nickel to 1 gram of pumice, or 10 per cent., it may be assumed for the purposes of the calculation that a uniform distribution has been obtained. If the quantity of promoter, for example, thoria, be taken at the optimum concentration, namely, 10–12 per cent. of the nickel (at. wt. 59), then if the whole of the thoria (mol. wt. 264) is deposited on the nickel, the surface covered by it will be approximately 1.40 that covered by the catalyst. An additional 1 per cent. of thoria will increase the surface area covered by it by 1.400 (approx.) and even with 100 per cent. of thoria present, the surface covered will be but 1.4 to 1.5 of the total.

Round the optimum concentration, therefore, marked changes in velocity with changes in concentration of promoters of high molecular weight would not be expected.

2. Different results are obtained when thoria replaces the pumice as carrier, and for the same catalyst space about five times the quantity of oxide is required. Thus assuming the nickel to be deposited entirely at the surface of the thoria, 0.1 gram of nickel on 5 grams of thoria, that is, 2 per cent., gives the same exposed surface of catalyst as 0.1 gram of nickel on 1 gram of pumice. A reduction, therefore, from 2.0 per cent. to 1.8 per cent. of nickel means a change in surface of 10 per cent., so that when the catalyst

is deposited at the surface of the promoter, small changes in the concentration of the former produce important alterations in the velocity of the reaction (compare Section B, The Incandescent Mantle).

Influence of Temperature.—Reference was made previously to the fact that nickel oxide to which chromium oxide had been added required a higher temperature of reduction than nickel oxide alone. It has been found that oxides capable of combining with nickel oxide under proper conditions, forming, for example, nickel chromate, exert their maximum catalytic effect at a higher temperature than does either nickel alone or nickel in conjunction with substances of the thoria type (see Table II). The following table shows the influence of temperature on the maximum catalytic effect of a nickel-thoria and a nickel-chromium oxide catalyst, respectively.

TABLE IV.

Temp.	Speed in c.c. min.		
	Ni-ThO ₂ .	Ni-Cr ₂ O ₃ .	Ni.
295°	590	550	32-35
280	600	220	"
270	600	62	27
250	330	24	"
200	86	Less than 10 c.c.	ca. 2
150	15	Not estimable	"

The reduction in speed shown in the case of the nickel-chromium oxide catalyst is greater than can be accounted for by the fall in temperature: alumina, silica, molybdenum oxide displayed the same comparative inertness below 270°.*

Typical analyses of the gases produced are given in the following table.

TABLE V.

	Ni alone.		Ni-Thoria. Temp. 270°.	Ni-Thoria. Temp. 180°.
	Temp. 280°.	Temp. 270°.		
	I.	II.		
Carbon dioxide	0.4	0.6	1.2	1.3
Carbon monoxide	0.3	0.9	0.5	0.8
Methane	31.6	31.2	30.7	
Hydrogen	67.2	67.2	67.4	
Total	99.5	99.9	99.8	

Carbon Dioxide and Hydrogen.—A few experiments have been carried out with these gases and the maximum velocities obtained at the optimum concentration of promoters are given in Table VI.

The temperature was 360—370° in all the experiments.

Probably compound formation of some type is taking place below this temperature.

TABLE VI.

Oxide.	Speed in c.c./min.	Oxide	Speed in c.c./min.
Thorium	550	Molybdenum	35
Glucinum	540	Vanadium.....	58
Chromium	490	Ni alone	43
Aluminium	450		

Table VII shows in greater detail the effect of the concentration of the oxides of thorium and glucinum on the speed.

TABLE VII.

Cone. as % of Ni present.	Speed in c.c./min.		Cone. as % of Ni present.	Speed in c.c./min.	
	ThO ₂ .	CO.		ThO ₂ .	CO.
0.1	50		10.0	550	260
0.5	62		20.0	540	540
1.0	80	60	30.0	—	490
5.0	270	—	50.0	520	

The results have been plotted in Fig. 1. The curves for glucinum oxide given by the two oxides of carbon lie close together, whilst small quantities of thoria do not exhibit the same accelerative power in the carbon dioxide-hydrogen reaction as in that involving the lower oxide.

B. *Applications of the Dehydration or Hydration Hypothesis.*

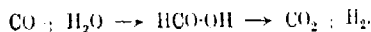
Promoters have been used in many catalytic reactions, and in considering the probable mechanism of their action on the diverse catalysts employed, it is necessary to deal with each reaction separately. The nature of the reacting substances, of possible intermediate compounds, and of end-products, and their action on the catalytic materials must be studied. In addition, optimum concentrations will differ with each catalyst and with the nature of the support, if any.

Action of Carbon Monoxide on Steam.

It has been stated previously that carbon monoxide reacts with steam as follows :



Armstrong and Hilditch (*Proc. Roy. Soc.*, 1920, [A], 97, 265) have advanced the theory that the effectiveness of copper as a catalyst in this reaction is due to its power of dehydrogenating formic acid, which they conceive to be the intermediate compound formed :

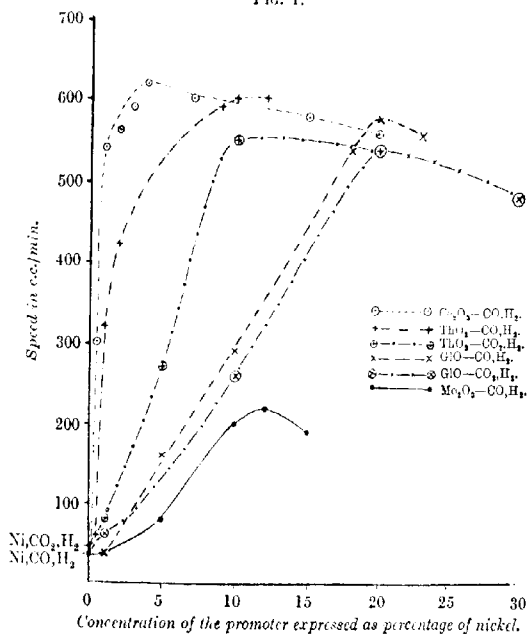


The Badische Co. have used nickel as a catalyst, and as this metal decomposes steam only slowly at a red heat, but dehydrogenates

formic acid rapidly at low temperatures, the mechanism of the process may be considered to be similar to that with copper.

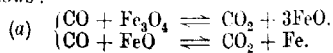
Further, the reversibility of the dehydration process in the case of ethyl alcohol in the presence of oxide catalysts has been demonstrated by Engelder, who was able to show that the alcohol-water-ethylene equilibrium could be displaced by the addition of water to the incoming alcohol (*J. Physical Chem.*, 1917, **21**, 676).

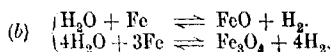
FIG. 1.



It will follow, then, from the conclusions of these authors that the presence of a hydrating agent such as alumina or thoria in contact with the catalyst, for example, nickel, will accelerate the velocity of the reaction by forming the intermediate compound, in this case formic acid, for decomposition by the catalyst.

In addition to copper, the action of iron oxide has been studied by Armstrong and Hilditch, who attribute the formation of carbon dioxide and hydrogen to alternate reduction and oxidation of the catalyst as follows:





The addition of promoters to the iron or iron oxide increases the velocity of this reaction to a marked extent, and among the most effective are hydrating agents and oxygen carriers. For example, with a mixture of iron oxide, chromium oxide, and thorium oxide, the velocity of this reaction is at least eight times as great as that with iron alone (compare Pease and Taylor, *loc. cit.*). On the assumption that reduction and oxidation are taking place only, the thorium oxide would appear to operate by adsorption of water vapour, thus producing a greater concentration of this gas at the surface of the catalyst. The chromium oxide may act in some way as an oxygen carrier, but more probably acts in a similar manner to thorium oxide.*

The remarkable increase in activity shown by iron in the presence of promoters, together with the known dehydrogenating action of this metal, suggests that the hydrogen is produced both through the formation of formic acid and through the reduction and oxidation of the catalyst. In any case, hydration occurs and the function of the promoter will be in part to do work—hydration—for which it is more suited than the iron.

The experiments to test these suggestions are still in an early stage, but sufficient evidence has been obtained to support the hypothesis.

Nickel and iron have been used as catalysts, and it has been found that the speed with nickel alone is greater than with iron alone at the temperature of 400–450°. The results with promoters show that the accelerative influence with iron as catalyst is proportionately far in excess of that with nickel, although the actual speeds obtained are in the reverse order. Further experiments on the effect of the addition of the same promoter to substances capable of catalysing the same reaction in varying degree are required before a general statement on this point can be made. This case must not be confused with that previously cited, in which two reactions are taking place simultaneously in the presence of the same catalyst.

It would be anticipated from the hypothesis, that a good dehydrogenating catalyst in contact with a good hydrating agent would give satisfactory results, and it is noteworthy that the majority of the catalytic materials patented by the Badische Co. for use in this reaction consists of such a mixture. The following may be

* In many oxidation experiments involving water, it has been shown that iron-thoria is more active than iron-chromium oxide; which would scarcely be the case if the promoter functioned by activating the oxygen.

quoted as examples: mixtures of oxides of iron, nickel, and cobalt with oxides of chromium and thorium; oxides of vanadium and chromium; oxides of manganese and chromium, of copper and zirconium, of lead and tungsten, and of cerium and chromium. A comparison of the results given by these mixtures would be of great value, in particular by the last-named; this consists of two excellent hydrating agents, which under suitable conditions act also as oxygen carriers.

The Incandescent Mantle.

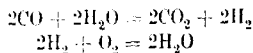
In general, an oxygen-carrier such as manganese dioxide, vanadium pentoxide, or cerium dioxide is used in conjunction with a base such as thoria, alumina, etc., in the making of a gas mantle. A mantle consisting of 0.9 per cent. of ceria together with 99.1 per cent. of thoria is the only one used extensively by reason of its high light emission, strength, and life.

Now, the oxidation of a hydrocarbon in the presence of a catalyst may be considered as taking place in two stages, namely, (1) the addition of oxygen to form an intermediate compound, and (2) decomposition of the latter to give carbon dioxide and water (compare Bone and collaborators, T., 1903 *et seq.*, for papers on the oxidation of hydrocarbons). Thus the maximum catalytic effect would in all probability be obtained by using a powerful oxygen carrier in conjunction with a strong dehydrating agent. Such a mixture as ceria-thoria fulfils these conditions, so that, in part, at all events, the superiority of this mixture may be attributed to the fact that the ceria acts as a promoter to the thoria, its particular function being to form the intermediate compound for dehydration by the thoria (compare Pease and Taylor, *loc. cit.*, who have also suggested that the ceria acts as a promoter). Further, the fact that the light emission falls when the content of ceria is increased above 1 per cent. may be explained on the assumption that the thoria acts, not only as a catalyst, but also as a carrier for the promoter, and, as shown previously (see Experimental part), under these conditions a small increase in the amount of the ceria present is sufficient to cover a large surface of the thoria.

The combustion of hydrogen may be explained on similar lines to those indicated above, but the mechanism of the oxidation of carbon monoxide appears to fall in a different category. Rideal and Taylor (*Analyst*, 1919, **44**, 89) have shown that the preferential combustion of small quantities of carbon monoxide in hydrogen does not take place through the operation of the water-gas reaction, $\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{H}_2 + \text{CO}_2$, at low temperatures, iron or copper, with chromium oxide and ceria or thoria added in small quantity,

being used as catalyst. It appears, however, somewhat difficult to account for the action of a poor oxygen activator such as thoria, and further it can be shown that with the same quantity and type of catalyst as was used in the preferential combustion experiments, the water-gas reaction takes place to an appreciable extent at 300°.

The combustion of carbon monoxide under higher temperature conditions than those used by Rideal and Taylor has been considered to take place through the action of the water present (Dixon, *Phil. Trans.*, 1884, **175**, 617; compare also von Wartenberg and Sieg, *Ber.*, 1920, **53**, [B], 2192) as follows :



in which case, the functions of the thoria and ceria are similar to those of the catalysts in the water-gas reaction. It is hoped to test the above suggestions experimentally in the near future.

Selective Catalysis.

In working on reactions similar to that of the synthesis of methane, where one or more intermediate compounds are assumed to be formed, it was thought that by adding a suitable substance in small quantity to the catalyst, it should not be impossible, provided the correct physical conditions were obtained, to prevent the reaction proceeding to the methane stage and to obtain interesting products. A few experiments were tried, but the results were entirely negative.

Rosenmund, Zetzsche, and Heise (*Ber.*, 1921, **54**, [B], 425), working on similar lines, found that by the addition of suitable promoters or inhibitors they were able to control the reduction of benzoyl chloride in the presence of palladium in such a manner that the chief product might be benzaldehyde, benzyl alcohol, benzyl benzoate, dibenzyl ether, or toluene. The regulating substances were chosen to contain an element of variable valency, but appear also to have contained one of the ordinary catalyst poisons; for example, quinoline heated with sulphur was most active.

Conclusion.

It has been shown in this paper that

(1) The action of promoters in the synthesis of methane from carbon monoxide and hydrogen, and carbon dioxide and hydrogen in the presence of nickel, depends on the dehydration of an unstable intermediate compound.

(2) Promoters may act selectively. The action of the promoters discussed may be classified temporarily as follows :

(i) The promoter decomposes intermediate compounds formed by the catalyst.

(ii) The promoter causes the reacting substances to combine, the resulting intermediate compound being decomposed by the catalyst.

(iii) The promoter adsorbs or combines with one of the reacting substances, producing a greater concentration of the latter at the surface of the catalyst.

The study of promoters is being continued partly on the lines indicated in this paper and partly with reference to those reactions involving direct hydrogenation of unsaturated compounds. The influence of groups such as OH, NH₂, etc., is being determined not only on the velocity of hydrogenation but also on the type of promoter required.

The work described above was carried out in the laboratories of the South Metropolitan Gas Company, and the author is indebted to the Directors of the Company and to E. V. Evans, Esq., Chief Chemist, for permission to publish the results. Thanks are due to H. Stanier, Esq., for much advice, and to Messrs. Townsend and Harvey for assistance in some of the experiments.

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[Received, March 20th, 1923.]

CLXX.—*The Mobility of Symmetrical Triad Systems,
Part II. The Conditions Relating to Systems
Terminated by the o-Phenylene Group. Derivatives
of Indene.*

By CHRISTOPHER KELK INGOLD and HENRY ALFRED PIGGOTT.

IN discussing the mobility of the systems reviewed in Part I (I., 1922, **121**, 2381), two classes of evidence were employed:

(A) Proof that two asymmetrically substituted derivatives, which, from the methods of their synthesis, should have formulae such as $C_6H_4Me \cdot N:N \cdot C_6H_5$ and $C_6H_5 \cdot NH:N \cdot N \cdot C_6H_4Me$, differing only in the position of the mobile hydrogen atom and double bond, are actually identical (symmetry test).

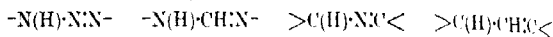
(B) Proof that this single individual behaves as if it were a mixture of the two forms that compose it, by giving four substances instead of two when treated with reagents that rupture the molecule, at the double bond (fission test).

To these we may now add a third class of evidence:

(C) Proof that the single individual referred to in (A) behaves as if it were a mixture of the two forms, by giving two isomeric substances such as $C_6H_4Me \cdot NR \cdot N \cdot N \cdot C_6H_5$ and $C_6H_5 \cdot NR \cdot N \cdot N \cdot C_6H_4Me$, when the mobile hydrogen atom is replaced by an alkyl or acyl group (substitution test).

It need scarcely be said that these three tests for mobility should support one another, as, actually, they invariably do.

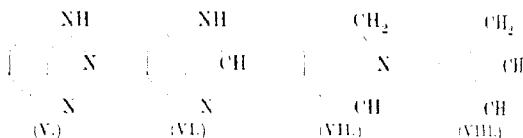
In Part I the four systems



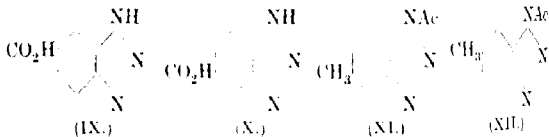
were examined as regards their mobility when terminated by two phenyl groups, and the conclusion drawn was that whereas diazoaminobenzene (I) and diphenylformamidine (II) are undoubtedly tautomeric, the systems present in benzyldenebenzylamine (III) and diphenylpropene (IV) are absolutely immobile; so much so that isomeric change could not be observed even at fairly high temperatures.



Having established these facts, it was decided to turn next to the corresponding series of cyclic structures in which the two phenyl groups of the first series are replaced by a single phenylene group. The four parent substances are therefore aziminobenzene (V), benziminazole (VI), *is*indole (VII), and indene (VIII).



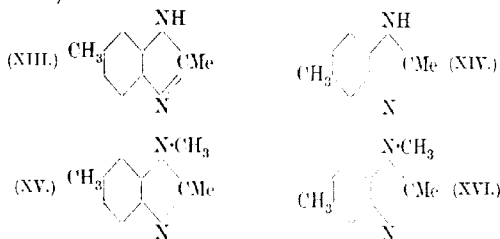
As regards the first of these, Griess at an early date drew the conclusion that aziminobenzene (V) is symmetrically constituted because two aziminobenzoic acids, which, from the mode of their preparation, should have the formulae (IX) and (X), were found to be identical (*Ber.*, 1882, **15**, 1878), a result which was subsequently



confirmed by Zincke and Helmert (*Annalen*, 1896, **291**, 313). Aziminobenzene satisfies, therefore, what we have called the

symmetry test (A), and although no suitable way of applying the fission test (B) has yet been found, it is interesting to note that the substitution test (C) is satisfied. Zincke and Lawson (*Annalen*, 1887, **240**, 119), by acetylation of aziminotoluene, obtained a mixture of two isomeric acetyl derivatives (XI and XII), which on hydrolysis gave back the same parent aziminotoluene. Zincke and Lawson themselves regarded the acetyl compounds as physical isomerides, but this they certainly are not, because they can co-exist in solution both at high temperatures and at the ordinary temperature. There can be no question but that they are structurally isomeric, and the fact that on hydrolysis they give the same aziminotoluene constitutes additional confirmation of the mobility of the three-nitrogen system present in that substance.

The same two types of evidence (A and C) support each other in proving the mobility of the triad system in benziminazole (VI). Thus the rational synthesis of the compounds (XIII) and (XIV) leads actually to a single individual which, on methylation, gives a mixture of two isomeric *N*-methyl derivatives (XV) and (XVI) (O. Fischer, *J. pr. Chem.*, 1906, [ii], **73**, 419; 1907, [iii], **75**, 88; and others).

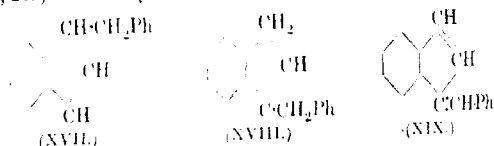


Up to this point, therefore, the parallelism with the open-chain series in which the triad system is terminated by two phenyl groups holds good: both in the open-chain and in the cyclic series the systems NH·N·N and NH·CH·N are actively tautomeric. Therefore, special interest attaches to the two remaining types (VII and VIII), containing the systems CH·N·C and CH·CH·C which are known to be inactive when terminated by phenyl groups. Unfortunately, it is not yet possible to complete the intended comparison, because, although indene (VIII) is the parent of a large and important series of compounds for which several general methods of preparation are known, neither *isoindole* (VII) nor any of its derivatives appears to have been prepared hitherto, and therefore it has become necessary, not only to synthesise *isoindole* itself and study its reactions, especially fission and substitution

reactions, but also to work out general methods for the preparation of derivatives suitable for the application of the various tests for mobility given on p. 1469. Thus we have been compelled to undertake a somewhat lengthy investigation of the chemistry of isoindole and its derivatives before making any attack on the special problem of the tautomeric mobility of the substance, and it has seemed desirable, therefore, in the meantime to push forward the projected series of experiments on the tautomeric mobility of indene. The results have justified this decision, for these experiments have yielded the first evidence of a marked difference between the structural conditions present in the open-chain and cyclic series. Unlike diphenylpropene, which is definitely static, indene is mobile, being strictly comparable in this respect with aziminobenzene and benziminazole.

It would be premature at the present stage to discuss the reason for this extraordinary contrast, and it is proposed to reserve the question until the intended comparisons have been completed; but it will be noted that the case of indene is a significant indication that the general conclusion, stated in Part I (*loc. cit.*, p. 2384), as to the structural conditions which determine mobility, although substantially correct as far as it goes,* must be regarded, nevertheless, as a very crude approximation only to the truth.

It is not necessary to enter in detail into the previous attempts which have been made to examine the mobility of indene by the symmetry method, because these attempts have invariably involved substitution in the three-carbon system itself. Thus Courtot (*Compt. rend.*, 1915, **160**, 523) showed that 1-benzylindene (XVII), prepared from benzyl chloride and magnesio-indene, is different from, but very easily convertible into, 3-benzylindene (XVIII), which Thiele and Bühner had previously obtained (*Annalen*, 1906, **347**, 249) from benzylideneindene (XIX) by reduction. No attempt

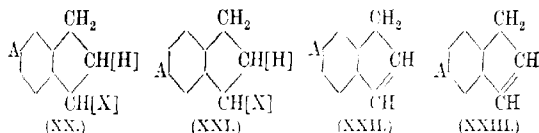


was made by Courtot to detect the reversibility of the interconversion which he had observed, and whether or no the benzylindenes are actually the individuals of a tautomeric system cannot be deduced from Courtot's work; but even if they are not, it would

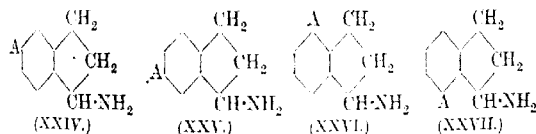
* For example, the discovery that the indene system is mobile is in keeping with the correlation indicated in Part I between mobility and capacity for β -kylation.

not follow that the unsubstituted three-carbon system present in indene itself is not mobile, because it has been shown (Bland and Thorpe, T., 1912, **101**, 871, 1740) that the presence of an α - or γ -benzyl group suppresses the mobility of the three-carbon system of glutaconic acid to a remarkable extent.

It is, however, quite unnecessary to tamper in any way with the three-carbon system of indene to obtain an experimental proof or disproof of its symmetry. One can proceed as follows: first, two substituted indanes, one a 1:5-derivative (XX) and the other a 1:6-derivative (XXI), are synthesised, and each of them is rigorously orientated; then, by elimination of the group $H-X$, each indane is converted into an indene which is substituted only in the benzene nucleus; the identity or non-identity of the mono-substituted indenenes (XXII and XXIII) thus obtained establishes the symmetry or dis-symmetry of the unsubstituted triad system present in the indene nucleus. This is the plan on which the present investigation has been based, and it may here be stated that the results clearly demonstrate the symmetry of the indene system.

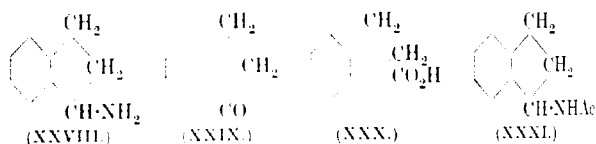


Our experiments have throughout been directed to the production of a pair of isomeric 1-hydrindamines, either of the types (XXIV) and (XXV), or of the types (XXVI) and (XXVII), from any of which ammonia could be eliminated to give substituted indenenes. With this object, a close study has been made of a considerable number of indanes in which the group A has been NO_2 , NH_2 , NHAc , OH , or Me , while the group X has been either NH_2 or some group which can readily be converted into an amino-group.



Kipping and Revis (T., 1897, **71**, 250) have shown that 1-hydrindamine itself (XXVIII) can be readily prepared by the reduction of the oxime of 1-hydrindone (XXIX), which, in turn, can be obtained by the action of aluminium chloride on the chloride of β -phenylpropionic acid (XXX). Our plan, therefore, was to carry

out a similar series of preparations starting with *o*-, *m*-, and *p*-substitution products of β -phenylpropionic acid. It will be observed, however, that whilst *o*- and *p*-substituted phenylpropionic acids can give rise respectively to 4- and 6-substituted hydrindones and hydrindamines only, *m*-substituted phenylpropionic acids, on the other hand, might yield 5- or 7-derivatives of indane. For this reason, and also because this method as a source of indanes is further greatly limited by the fact that the chlorides of substituted phenylpropionic acids do not always undergo internal condensation in presence of aluminium chloride as readily as does β -phenylpropionyl chloride itself,* it became necessary at an early stage of this investigation to discover a means of supplementing existing synthetical processes by finding some new sources of substituted 1-hydrindamines. The direct introduction of substituents into 1-hydrindamine itself and into 1-hydrindone appeared to offer possible methods of preparing the required isomeric hydrindamines, and therefore a preliminary investigation was commenced with a view to the preparation of substituted hydrindamines and hydrindones directly from the parent substances. The tracing out of the inter-relationship and the orientation of the series of substances produced by these means have proved a tedious, and, in some respects, an intricate task, but it has at length been completed, and has resulted finally in the synthesis of a pair of isomerides of the type required.

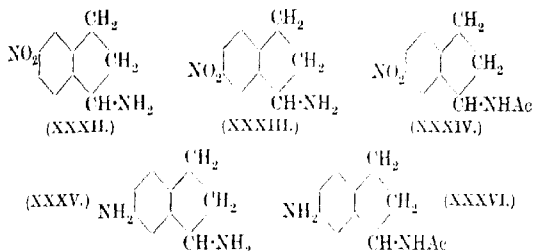


It is well known that aniline, on nitration in concentrated sulphuric acid, yields a meta-substitution product, whilst acetanilide under similar conditions gives a para-compound. Therefore one of the first plans tried consisted in directly nitrating 1-hydrindamine and its acetyl derivative (XXXI): for, if there were any difference between the directive influence of the aminosulphonic and acetyl-amino-groups, these reactions should lead to two nitrohydrindamines (XXXII and XXXIII) having the required relationship

* For instance, the chloride of *p*-nitrophenylpropionic acid (LXXI) on treatment with aluminium chloride yields *p*-nitrophenylpropaldehyde (LXXII), and no trace of the expected hydrindone derivative (compare p. 1505).

(LXXI) NO_2 $\text{CH}_3\text{CH}_2\text{CO}_2\text{H}$ NO_2 $\text{CH}_3\text{CH}_2\text{CHO}$ (LXXII)

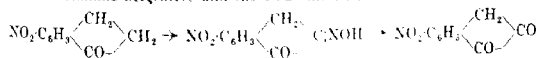
to each other. It was found, however, that the nitration product of acetylhydrindamine, now known to have formula (XXXIV), was identical with the acetyl derivative of the nitration product (XXXIII) of hydrindamine itself. The nitro-compounds (XXXIII) and (XXXIV) yielded, on reduction, amino-compounds (XXXV) and (XXXVI), on the identification of which the orientation of this series as 6-substituted-1-hydrindamines depends (*v. infra*).



The second starting point was 1-hydrindone, the nitration of which was attempted by Kipping, who obtained, under conditions which he himself found difficult to reproduce, a very impure product, containing, however, a crystalline nitrohydrindone. This substance, when pure, melted at 76–77°, but it was obtained only in small quantities and was difficult to purify (T., 1894, 65, 495), so that no attempt was made to determine the position of the nitro-group or to characterise the substance by the preparation of derivatives. More recently (*Ber.*, 1916, 49, 1279), von Braun and Heider carried out the same nitration, but did not try to purify the product.*

We have carefully examined the nitration of 1-hydrindone, and have evolved a process by means of which it is possible to obtain a quantitative yield of a mixture of two mononitrohydrindones, which, owing to their extraordinary tendency to crystallise from solvents, may readily be separated from one another and obtained in a pure condition. The two substances melt at 74°

* These investigators converted the crude nitration product successively into the oximino-derivative and the 1:2-diketone.



but it may be doubted whether they obtained either the oximino-compound or the diketone in a pure condition, for it is shown in this paper that the original nitration product is a mixture of isomerides. Since the corresponding oximino-compounds melt with decomposition, and the diketones decompose before they melt, mixtures of isomerides would not be easy to recognise.

and 77°, respectively, and it is probable that the latter is the substance isolated by Kipping.

The orientation of these substances practically resolves itself into deciding whether they are 6- or 4-nitrohydrindones, and this was readily accomplished by oxidation. It is well known that 1-hydrindone, on oxidation with cold alkaline permanganate, gives phthalic acid. If, however, dilute chromic acid is employed, homophthalic acid (XXXVIII) may be obtained as the main product, phthalic acid being produced in small amount only. Exactly similar results were obtained using the nitrohydrindone having m. p. 74°. Cold alkaline permanganate converted it into 4-nitrophthalic acid (XXXIX), which has been well characterised by other workers, and was readily identified. On the other hand, dilute chromic acid gave, in addition to a small amount of 4-nitrophthalic acid, a large yield of 4-nitrohomophthalic acid (XL), the constitution of which follows first from the fact that it is practically the sole mononitration product of homophthalic acid itself, and secondly from the fact that on further oxidation it gives 4-nitrophthalic acid. This relationship between the nitro-ketone and the two nitro-acids was further confirmed in two ways. In the first place, the nitro-ketone was converted into its oximino-derivative (XLI) by treatment with anhydrous nitrate and hydrochloric acid, and the oximino-compound hydrolysed by hydrochloric acid and formaldehyde (compare Perkin, Roberts, and Robertson, *T.*, 1912, **101**, 234) to the corresponding 1:2-diketone (XLII). This substance, on oxidation with dilute chromic acid, passed smoothly into 4-nitrohomophthalic acid. The second method consisted in first converting the nitro-compound into its 2:2-dibromo-derivative (XLIII), and then oxidising this with permanganate to 4-nitrophthalic acid. It is evident, therefore, that the nitro-compound having the m. p. 74° must be 6-nitro-1-hydrindone (XXXVII). The various relationships are summarised in Table I.

Having orientated 6-nitrohydrindone, it then became possible by establishing a connecting link with the nitration products obtained from hydrindamine and acetylhydrindamine, to orientate these substances. The nitro-ketone (XXXVII), or its dibromo-derivative (XLIII) was first reduced by means of stannous chloride to the amino-ketone (XLIV), which was then acetylated, and the acetyl derivative (XLV) converted into its oxime (XLVI). This substance on reduction gave an acetyl derivative (XLVII) of amino-hydrindamine, which on further acetylation gave a diacetyl compound (XLVIII), identical with the product of acetylation of the compounds (XXXV) and (XXXVI), derived by the reduction of the nitration products both of hydrindamine and acetylhydrind-

amine. Evidently, therefore, all these substances are 1:6-disubstituted indanes (see Table II).

TABLE I.

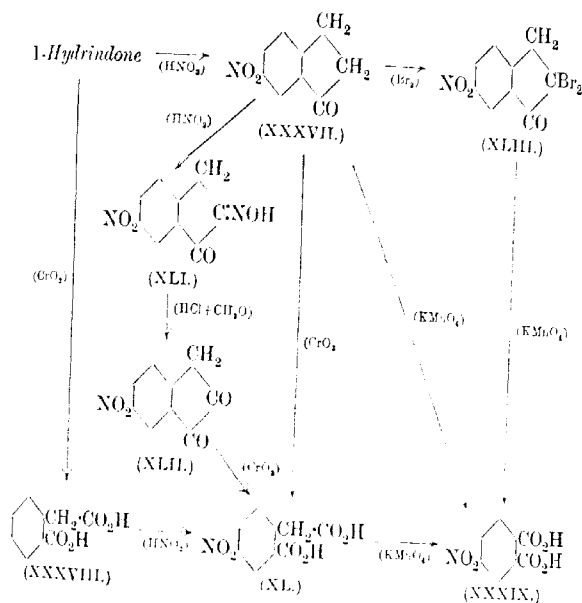
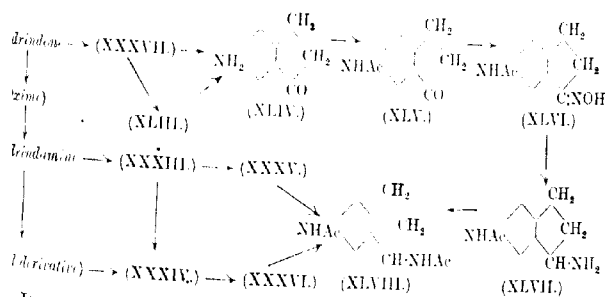


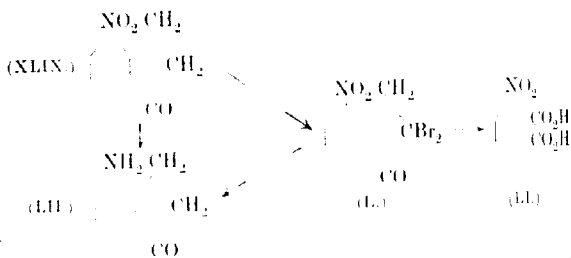
TABLE II.



It was necessary to work through this somewhat lengthy series of reactions in order to establish the connexion between the two

series, because, curiously enough, the oxime of 6-nitrohydrindone (XXXVII), on reduction, even under conditions in which water was excluded as completely as possible, yielded the amino-ketone (XLIV), and not, as was at first hoped, the aminohydrindamine (XXXV).

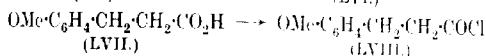
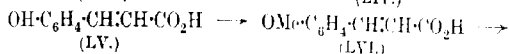
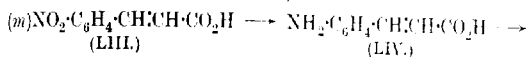
The second isomeric nitrohydrindone (m. p. 77°) proved on examination to be a remarkably stable molecular compound of 6-nitrohydrindone and 4-nitrohydrindone (XLIX)*. Not only was it incapable of being resolved into the simple ketones by fractional crystallisation, either from solvents or from the molten substance, but it also yielded a single oxime and semicarbazone, from both of which it could be regenerated, whilst fractional oxime- and semicarbazone-formation had no effect on its melting point or crystallographic homogeneity. On bromination, however, it yielded a mixture of 2:2-dibromo-6-nitro-1-hydrindone (XLII) and the isomeric 2:2-dibromo-4-nitro-1-hydrindone (L), the structure of which is indicated by its oxidation by permanganate to 3-nitrophthalic acid (LI). Similarly, on reduction, the nitro-ketone (m. p. 77°) yields a mixture of 6-aminohydrindone and its isomeride, 4-amino-1-hydrindone (LII). The latter may also be obtained by reduction of the dibromonitro-compound (L), and its orientation follows from this fact:



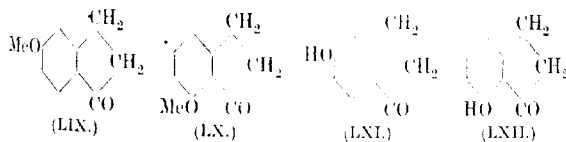
It may be noted in passing that, owing to the fact that 4-aminohydrindone is much more soluble than 6-aminohydrindone, and that 4-nitrohydrindone forms only one-sixth of the mononitration product of 1-hydrindone, it is unnecessary to separate the nitro-ketones when preparing the 6-amino-ketone, which may be obtained directly by reduction of the crude nitration product, the isomeric amino-ketone remaining in the mother-liquors. This circumstance renders 6-amino-1-hydrindone the most easily available of all the 6-substituted indanes described in this paper (*cf. infra*).

* The formation of molecular compounds in the hydrindone series seems not uncommon. 6-Methoxy-1-hydrindone forms a molecular compound with its own oxime (compare p. 1492).

Whilst these experiments on the production of 1:4- and 1:6-disubstituted indanes were in progress, a second series of experiments was started with the object of working out methods for the preparation of isomeric 1:5- and 1:7-derivatives. After a number of unsuccessful experiments, a satisfactory starting point was found in *m*-methoxy- β -phenylpropionic acid (LVII), which can be prepared, following the procedure described in the experimental part of this paper, from *m*-nitrocinamic acid (LIII) by reducing this with stannous chloride, diazotising the tin double salt of the base (LIV), decomposing the product with boiling water, methylating with methyl sulphate the phenolic acid (LV) thus obtained, and then reducing the unsaturated methoxy-acid (LVI) to the corresponding saturated acid (LVII) :



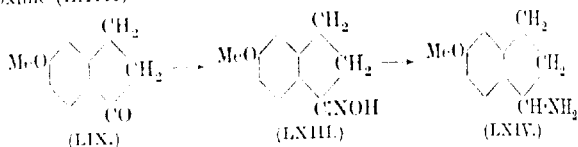
It will be evident that the chloride (LVIII) of this acid might give rise either to 5-methoxy- or 7-methoxy-1-hydrindone (LIX or LX) when internally condensed by means of aluminium chloride. Actually the condensation gave an excellent yield of a single methoxy-ketone together with a phenolic by-product consisting of two isomeric substances which were readily identified as 5-hydroxy-1-hydrindone (LXI) and 7-hydroxy-1-hydrindone (LXII), both of which have been described by Auwers and Hilliger (*Ber.*, 1916, 49, 2410). The methoxy-ketone was readily identified as 5-methoxy-1-hydrindone (LIX) by preparing it from 5-hydroxy-1-hydrindone by methylation with methyl sulphate in alkaline solution. Furthermore, the methoxy-ketone on oxidation by means of chromic acid yields a methoxyhomophthalic acid (compare p. 1476) together with 4-methoxyphthalic acid, which has previously been characterised.



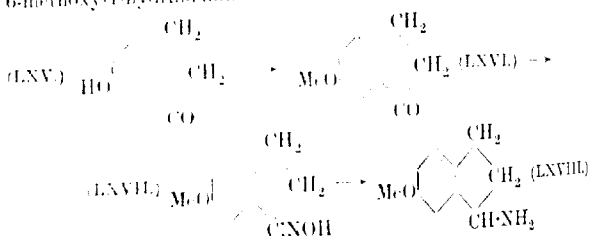
At this point in the general investigation it became evident that, whilst the first series of experiments, starting from hydrindamine and hydrindone, was leading mainly to 1:6-derivatives, the 1:4-isomerides being produced in small amount only, the

second series, starting from *m*-nitrocinnamic acid, was leading mainly to 1:5-disubstituted indanes, and only to a small extent to the 1:7-isomerides. This at once settled the question as to the orientation of the isomeric hydrindamines which were to be synthesised for conversion into possibly identical indenenes, and it was decided now to employ the information which had been gained regarding the synthetic methods available for the preparation of 1:5- and 1:6-disubstituted indanes in order to complete the synthesis of a pair of isomeric 5- and 6-substituted hydrindamines. The starting points selected were the representative in each series which had been found to be easily obtainable in the pure condition and in large quantities, namely, 5-methoxy-1-hydrindone (LIX) and 6-amino-1-hydrindone (XLIV).

The conversion of 5-methoxy-1-hydrindone into 5-methoxy-1-hydrindamine (LXIV) was readily accomplished by reducing the oxime (LXIII) with sodium amalgam and acetic acid:

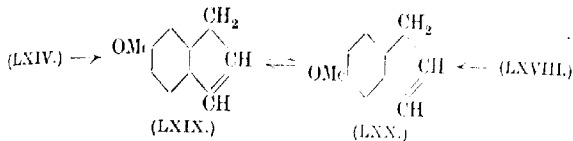


6-Amino-1-hydrindone was now converted into 6-methoxy-1-hydrindamine (LXVIII) in the following steps. The amino-ketone was first diazotised under conditions carefully regulated so as to avoid the introduction of an oximino-group into position 2, and the 6-hydroxy-1-hydrindone (LXV) thus obtained methylated with methyl sulphate. The methoxy-ketone (LXVI) was then converted into the methoxy-ketoxime (LXVII), which, on reduction, yielded 6-methoxy-1-hydrindamine:



It need scarcely be said that the two methoxyhydrindamines (LXIV and LXVIII), as well as the methoxy-ketoximes, the methoxy-ketones, and the hydroxy-ketones of the 5- and 6-substituted series, were found to be different from one another. Nevertheless, the two methoxyhydrindamines, when converted into

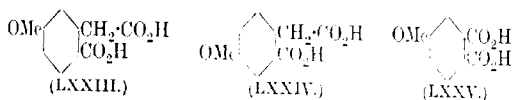
their salts, readily lost ammonia, yielding the same methoxyindene (LXIX or LXX) :



The formation of the indene takes place with quite remarkable ease. Thus the hydrochlorides of the two hydrindamines, on melting in the absence of any reagent, give an immediate precipitate of ammonium chloride, from which the indene may be removed by filtration or distillation. It was characterised by its boiling point, crystalline picrate, and crystalline dibromide.

Plainly, therefore, the triad system in indene satisfies what we have called the symmetry test (test *A*) for mobility. It remains now to describe the experiments which have been carried out with a view to apply the fission test (*B*) and the substitution test (*C*).

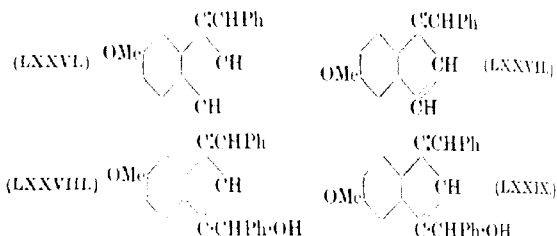
In the first place, it was anticipated (test *B*) that the indene on oxidation should give a mixture of 5-methoxy- and 4-methoxyhomophthalic acid (LXXIII and LXXIV) along with 4-methoxyphthalic acid (LXXV).



The experiment proved to be a difficult one, however, and although it was found possible to obtain a partly crystalline oxidation product by the use of cold dilute chromic acid, only two of the three acids mentioned above could be isolated in a condition of purity, namely, 5-methoxyhomophthalic acid (LXXIII) and 4-methoxyphthalic acid (LXXV). A third acid appeared to be present, but it could not be freed from 4-methoxyphthalic acid. Since 6-methoxy-1-hydrindone (LXVI), which on oxidation by hot chromic acid would be expected (p. 1476) to yield the two acids (LXXIV) and (LXXV) as sole products, was found to yield a very similar mixture from which the phthalic acid (LXXV) alone could be isolated in a condition of purity, we are of the opinion that the homophthalic acid (LXXIV) is actually produced by oxidation of the indene, but that owing to its similarity in solubility to 4-methoxyphthalic acid, and also because the separation is rendered more difficult by the presence of large quantities of amorphous products, we were not able to isolate it from the somewhat limited quantity of material at our disposal.

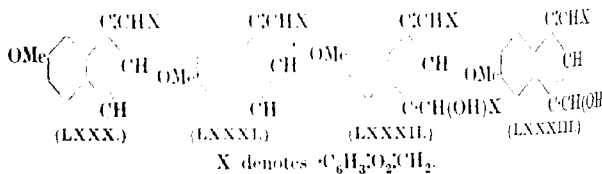
The orientation of 5-methoxyhomophthalic acid (LXXIII) follows from the fact that this acid is produced along with 4-methoxyphthalic acid (LXXV) by the action of hot chromic acid on 5-methoxyhydrindene (LIX). 4-Methoxyphthalic acid has previously been prepared and has been characterised by other workers.

Experiments on the application of the substitution test (C) yielded interesting results. One of the simplest ways of replacing the potentially mobile hydrogen atoms in the indene appeared to be to condense it with benzaldehyde, which, it was expected, would give rise to a mixture of two benzylideneindenes (LXXVI and LXXVII), or, possibly, the hydroxybenzyl derivatives of these substances (Thiele and Bühner, *Annalen*, 1906, **347**, 268) namely the compounds (LXXVIII) and (LXXIX):



Actually a mixture of two substances corresponding in composition with the compounds (LXXVIII) and (LXXIX) was obtained, but in this case also, owing to the similar solubilities of the compounds, it was found possible to isolate only one of them in the pure condition.

When benzaldehyde was replaced by piperonal a mixture was obtained which was readily separated by fractional crystallisation into two pure constituents, doubtless represented by the two formulae (LXXX) and (LXXXI), together with a mixture of less fusible substances having the composition of the compounds (LXXXII) and (LXXXIII), one of which was isolated in a state of purity.*



* Geometrical isomerism has never been previously observed amongst alkyld-indenes, and therefore it is very improbable that it is the cause of the formation of the pairs of isomers mentioned.

From these experiments, it follows that the three-carbon system in the indene nucleus is a mobile system, and, since it satisfies the test of symmetry, of substitution, and in all probability that of fission also, it must be regarded as in every way comparable with the mobile systems present in benziminazole and azimino-benzene, the evidence now provided being strictly parallel to that supplied by O. Fischer in the one case, and by Griess and Zincke in the other.

EXPERIMENTAL.

1-Hydrindone (XXIX).—The 1-hydrindone required for these experiments was prepared from β -phenylpropionyl chloride by internal condensation in the presence of aluminium chloride. The improved modification (Ingold and Thorpe, T., 1919, **115**, 149) of the original process described by Kipping (T., 1894, **65**, 4) was closely adhered to excepting in the following respect. It was found that by employing very finely ground aluminium chloride, instead of the ordinary form, the production of ketone took place almost quantitatively and in the course of a few seconds. It was necessary to use a large flask in order to prevent loss of material during the very sudden evolution of hydrogen chloride. On adding ice, a large proportion of the 1-hydrindone formed crystallised, but it was found convenient to isolate the whole together by extraction with ether, from which on evaporation it was obtained in a very pure form, so that purification by the tedious process, hitherto used, of distilling in steam was unnecessary. The average yield was 90 per cent. of the theoretical.

1-Hydrindamine (XXVIII).—The hydrindamine required was prepared by reduction of 1-hydrindoxime exactly as described by Kipping and Revis (T., 1897, **71**, 250).

(4) 4- and 6-Substitution Products of 1-Hydrindamine and 1-Hydrindone.

Nitration of 1-Hydrindamine.—This was best carried out by decomposing hydrindamine nitrate with cold concentrated sulphuric acid.

1-Hydrindamine Nitrate.—An aqueous suspension of 1-hydrindamine was exactly neutralised with dilute nitric acid, and the solution evaporated to dryness. The product separated from water in colourless needles, m. p. 135–138° (decomp.).

6-Nitro-1-hydrindamine (XXXIII). The nitrate (11 grams) was very gradually stirred in to 25 c.c. of concentrated sulphuric acid at –5° to 0°. (The addition of this quantity should occupy not less than thirty-five minutes, since, if it is performed too rapidly,

much decomposition will occur.) The mixture was kept for a further thirty minutes at -10° to -5° , allowed to warm to 0° , and poured into 80 c.c. of ice-water, from which, on standing, 6-nitro-1-hydrindamine sulphate crystallised in aggregates of minute needles. These were separated and decomposed with sodium hydroxide, which precipitated the free base as an oil, which rapidly solidified and on crystallisation from very dilute alcohol yielded very pale yellowish-green laminae, m. p. 40° . These, on keeping in the atmosphere for a short time, became opaque and then melted at $50-55^{\circ}$. The crystals were therefore dehydrated in an evacuated desiccator over potassium hydroxide, and the anhydrous material crystallised from dry ether, from which it separated in colourless, elongated prisms, m. p. $60-61^{\circ}$ (Found: C = 60.35; H = 6.0. $C_9H_{10}O_2N_2$ requires C = 60.64; H = 5.66 per cent.). A further quantity was obtained, mixed with a little hydrindamine hydrochloride, by decomposing the mother-liquors with the theoretical amount of barium chloride, filtering from the precipitated barium sulphate, and evaporating the filtrate to dryness. The solid residue, on a single crystallisation from water, deposited the hydrochloride of the nitro-base in a state of purity. The total yield was 85 per cent. of the theoretical.

The substance melting at 40° appeared to be an unstable hydrate. The actual melting point varied with the proportion of alcohol in the solvent, and only when much water was present was a well-defined substance obtained.

The *acetyl* derivative (XXXIV) was prepared by shaking a suspension of the base in aqueous sodium hydroxide with a small excess of acetic anhydride. It separated from alcohol or dilute acetic acid in small, colourless needles, m. p. 180° (Found: C = 59.99; H = 5.49. $C_{11}H_{12}O_3N_2$ requires C = 59.92; H = 5.49 per cent.).

1-Acetylaminoindane (Acetylhydrindamine) (XXXI).—This substance was prepared from hydrindamine exactly as in the case of the above nitro-derivative. It separated from dilute alcohol or dilute acetic acid in colourless prisms, m. p. 120° (Found: C = 75.39; H = 7.77. $C_{11}H_{13}ON$ requires C = 75.38; H = 7.48 per cent.).

Nitration of Acetylhydrindamine.—The *acetyl* derivative (3 grams) was added gradually to 25 c.c. of fuming nitric acid at 10° , and the solution kept for ten minutes and then poured into 150 c.c. of cold water. On adding excess of sodium hydroxide, the nitroacetyl-amino-compound slowly separated in a yield (3.1 grams) amounting to 82 per cent. of the theoretical. It crystallised from alcohol in colourless needles, m. p. 180° , and was easily identified as the 6-nitroacetyl compound (XXXIV) described above (Found:

C = 59.75; H = 5.58 per cent.). No other isomeride appeared to be present in the crude nitration product.

6-Amino-1-hydrindamine (XXXV).—6-Nitro-1-hydrindamine (2 grams) was dissolved in a solution of stannous chloride (8 grams of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ in 8 c.c. of hydrochloric acid). The reduction occurred with rise of temperature, and was completed by heating the solution to its boiling point. After cooling, the solution was diluted to 150 c.c. and the tin removed as sulphide. The filtered solution, on evaporation, left a very soluble crystalline hydrochloride, which on treatment with 50 per cent. aqueous potassium hydroxide yielded a colourless, crystalline base. This could not be satisfactorily crystallised, and therefore was characterised by conversion into its *diacetyl* derivative, m. p. 225°, which was found to be identical with the 1 : 6-diacetyl derivative described on p. 1491.

Nitration of 1-Hydrindone.—1-Hydrindone can be mononitrated by means of fuming nitric acid (*d* 1.5), but the product is contaminated by tarry substances, which render purification very difficult. However, by using potassium nitrate and sulphuric acid under the conditions described below, the reaction can be caused to proceed smoothly and without the formation of tars.

Potassium nitrate (10 grams), dissolved in 30 c.c. of concentrated sulphuric acid, was added in small portions at short intervals to a solution of 12 grams of 1-hydrindone in 100 c.c. of sulphuric acid, previously cooled to 0°. During the nitration the temperature usually rose to about 5°, but its exact regulation did not appear to be a matter of importance, provided that at no time did it rise above 15°. Nitrations carried out at -15° to -10°, 0° to 5°, and 10° to 15° gave similar and equally satisfactory results. After the addition of the nitrate had been completed, the flask containing the mixture was kept in ice for an hour. The contents were then poured on to crushed ice and the nitro-ketenes were collected by filtration after the excess of ice had melted.

For the separation of the two nitro-ketenes, m. p. 74° and 77°, the dried product of several nitration experiments was extracted with successive quantities of about 2.5 litres of boiling light petroleum (b. p. 50–60°). The first few extracts contained nearly the whole of the less fusible substance, and, on cooling, deposited a mixture of the two isomerides, whilst the mother-liquors, on evaporation, yielded the less fusible nitrohydrindone in an almost pure condition. It was finally purified by crystallisation from ethyl alcohol. The later petroleum extracts contained principally the more fusible nitrohydrindone and deposited this substance on cooling. The first crops of crystals from the earlier extracts and the residues obtained from the mother-liquors of the later extracts were then

combined and subjected to a similar process of separation. The progress of the separations was readily followed by inspection owing to the characteristic and widely differing appearance of the two isomerides.

6-Nitro-1-hydrindone (XXXVII).—This substance separates from light petroleum, alcohol, or ethyl acetate in large, thin leaflets. Very occasionally, however, it separates from light petroleum in slender, silky needles, which mat together, giving the substance the appearance and texture of glass wool. These two crystalline forms give identical solutions, and each, as well as a mixture of the two, melts at 74° . Further fractional crystallisation and regeneration from the oxime and semicarbazone do not change this melting point. The substance is rather sparingly soluble in light petroleum, but readily soluble in methyl alcohol, ethyl alcohol, or ethyl acetate, and very soluble in ether, benzene, or chloroform. It is very slightly soluble in water, but the solubility is not increased by adding sodium carbonate or sodium hydroxide, although, after a short time in the cold, and almost immediately on warming, decomposition sets in with the formation of tarry matter. The nitro-ketone is also unstable towards acids. It dissolves in concentrated sulphuric acid, giving a deep yellow solution from which the unchanged nitro-ketone may be recovered by adding water at once; on keeping for a few hours, however, a crystalline but complex and very insoluble substance, probably of the anhydrobishydrindone type, separates. The same or a similar substance is obtained if the nitro-ketone is boiled with concentrated hydrochloric acid for a few minutes, or if it is heated at 180° with 1 per cent. phosphoric acid. Heating with water alone in a glass tube causes the formation of tars, probably owing to the action of the alkalis dissolved from the glass. The nitro-ketone may be heated at 160° for ten minutes with 1 per cent. phosphoric acid and may be boiled for the same length of time with 10 per cent. hydrochloric acid without any appreciable conversion into the insoluble compound. The nitro-ketone is considerably more soluble in hydrochloric acid than in water. It gives no coloration with aqueous-alcoholic ferric chloride (Found: C = 61.0; H = 4.2. $C_9H_7O_2N$ requires C = 61.0; H = 4.0 per cent.).

The *oxime* was prepared by mixing a solution of the nitro-ketone (1.5 grams) in 20 c.c. of absolute alcohol with hydroxylamine hydrochloride (0.7 gram), and sodium carbonate (0.5 gram) dissolved in 7 c.c. of water. Twenty-four hours later, the solution was mixed with twice its bulk of water, and the precipitated oxime collected, washed with cold water, dried, and purified by crystallisation from ethyl acetate, from which it separated in prisms melting

at 193—195° (Found : N = 14.7. $C_9H_8O_3N_2$ requires N = 14.6 per cent.).

When the purified oxime was dissolved in boiling 10 per cent. hydrochloric acid, the ketone quickly separated as an oil, which solidified on cooling. Without purification, it melted at 73—74°, and on crystallising from petroleum was obtained in the usual characteristic flakes, m. p. 74°. On reduction with zinc and acetic acid, the oxime yielded 6-amino-1-hydrindone (p. 1488).

The semicarbazone separated almost at once when an alcoholic solution of the ketone was mixed with an aqueous solution of semicarbazide acetate. It was very insoluble and a solvent could not be found from which it could conveniently be crystallised, although it dissolved appreciably in boiling aniline. It was prepared for analysis by washing with boiling water and boiling alcohol (Found : N = 24.0. $C_{10}H_{10}O_3N_4$ requires N = 23.9 per cent.). When heated, it decomposed, without melting, at about 240°.

On boiling with a large excess of 10 per cent. hydrochloric acid, the semicarbazone dissolved, and although only a part of the ketone thus formed separated on cooling, by extracting with pure ether it was recovered almost quantitatively. Without purification, it melted at 72.5—74°, and after crystallisation from light petroleum, at 74°.

2:2-Dibromo-6-nitro-1-hydrindone (XLIII).—The nitro-ketone (5 grams) was dissolved in 15 c.c. of chloroform and treated at 0° with 36 c.c. of a solution of bromine in chloroform (250 grams per litre), which was added drop by drop as decoloration took place. The first drop took an appreciable time to react, but afterwards decoloration was almost instantaneous until nearly four atoms of bromine had been added, at which point there was appreciable diminution in the speed of absorption. Throughout the process, except for a short time at the commencement, hydrogen bromide was evolved. On evaporation of the solvent, a solid residue was obtained which, after recrystallisation from alcohol or ethyl acetate, melted at 112°. The dibromo-compound forms large, stout, well-defined prisms which are very soluble in cold chloroform, but only sparingly soluble in ether, ligroin, or cold alcohol (Found : Br = 47.6. $C_9H_3O_3NBr_2$ requires Br = 47.7 per cent.). On oxidation with alkaline permanganate, it gives 4-nitrophthalic acid (p. 1499), and on reduction by tin and hydrochloric acid or by zinc and glacial acetic acid it is converted into 6-amino-1-hydrindone (p. 1488). No reduction takes place when it is warmed with sodium iodide and acetic acid, and it was not found possible to obtain 6-nitro-1-hydrindone by partial reduction.

2-Oximino-6-nitro-1-hydrindene (XLI).—This substance was formed

with evolution of heat when concentrated hydrochloric acid (0.6 gram) was added to a warm solution of 6-nitro-1-hydrindone (3 grams) and isoamyl nitrite (3 grams) in absolute ethyl alcohol (20 c.c.). The temperature of the liquid gradually rose to the boiling point and the oximino-compound crystallised from the boiling solution. After keeping at 0° for half an hour, it was collected and recrystallised for analysis from ethyl alcohol. The yield was 80–90 per cent. of the theoretical (Found: $N = 13.4$. $C_9H_6O_4N_2$ requires $N = 13.6$ per cent.). 2-Oximino-6-nitro-1-hydrindone is moderately soluble in glacial acetic acid, sparingly soluble in cold alcohol, and only moderately soluble at the boiling temperature. It separates from alcohol in small, glistening plates, and from acetic acid in small, dense prisms which melt with decomposition at about 240°, the exact temperature depending on the rate of heating. With alkali hydroxides, it gives deep purple solutions which rapidly turn brown. The action of hydrochloric acid in the presence of formaldehyde is described below.

6-Nitro-1:2-diketohydrindene (XIII).—One gram of the finely powdered oximino-compound (above) was suspended in 2 c.c. of 40 per cent. formaldehyde and treated for two minutes with a rapid stream of gaseous hydrogen chloride, the tube containing the reaction mixture being immersed in water at 20°. The temperature of the suspension rose to 40°, whilst the suspended solid changed considerably in appearance. After keeping for a further two minutes, 4 c.c. of water were added, and the whole was cooled to 0° and filtered. The yield was 70–80 per cent. of the theoretical.

6-Nitro-1:2-diketohydrindene is a pale orange-brown, crystalline powder (minute needles), which, on heating to about 150°, carbonises and evolves gas. Although distinctly crystalline, and of homogeneous appearance under the lens, it does not separate well from the usual solvents. It is soluble in alkali hydroxides and carbonates, giving deep brown, unstable solutions which, on treatment with oxidising agents, yield amorphous products. Oxidation of the diketone itself by means of chromic acid leads to the formation of 4-nitrohomophthalic acid (Found: $N = 8.1$. $C_9H_5O_4N$ requires $N = 7.3$ per cent.).

6-Amino-1-hydrindone (XLIV). This substance has been prepared in the following ways:

(i) *Reduction of the crude nitration product of 1-hydrindone.* A boiling solution of the crude mixture of nitro-compounds (42 grams) in 95 per cent. ethyl alcohol (150 c.c.) was treated with an alcoholic solution of stannous chloride, made by dissolving 168 grams of the dihydrate ($SnCl_2 \cdot 2H_2O$) in a mixture of 160 c.c. of concentrated hydrochloric acid and 200 c.c. of 95 per cent. alcohol. The reducing

solution was added at such a rate that the heat evolved maintained the liquid just at the boiling point. After the addition was completed, the solution was evaporated to 100 c.c., cooled, and the double tin salt which had separated collected and decomposed by dissolving in hot water and pouring into concentrated aqueous sodium hydroxide in sufficient excess to keep all the tin in solution as sodium stannate. On cooling, a pale yellow substance separated which consisted essentially of 6-amino-1-hydrindone. This was collected by filtration, and the filtrate, which contained a mixture of the 6- and 4-amino-ketones, was worked up along with the aqueous alcoholic mother-liquors from the double tin salt. These were evaporated to small bulk, poured into an excess of concentrated sodium hydroxide, and, after combining with the other alkaline solution, extracted twenty times with an equal volume of ether. The ethereal solution was then extracted with successive small amounts of dilute hydrochloric acid, from which the free bases were subsequently precipitated by adding ammonia. The amino-ketone (15 grams) obtained from the crystallised tin salt consisted of almost pure 6-amino-1-hydrindone, and after crystallisation from alcohol melted at 171° . The base (6.5 grams) obtained from the ether extract was a mixture from which the same amino-ketone could be isolated by crystallising several times from alcohol.

(ii) *Reduction of 6-nitro-1-hydrindone.* This reduction was carried out like the previous one. In this case, however, the base obtained from the ethereal extract, as well as that from the crystallised tin salt, consisted of almost pure 6-amino-1-hydrindone, the yield being 70 per cent. of the theoretical.

(iii) *Reduction of 2:2-dibromo-6-nitro-1-hydrindone.* A solution of stannous chloride (8.3 grams of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$) in a mixture of alcohol (16 c.c.) and concentrated hydrochloric acid (10 c.c.) was added drop by drop to a solution of the bromo-ketone (2.5 grams) in 30 c.c. of boiling absolute alcohol. The resulting solution was evaporated almost to dryness, mixed with 10 c.c. of water, and poured into an excess of 30 per cent. aqueous sodium hydroxide. The base was extracted with ether, and then withdrawn from the ether by shaking with dilute hydrochloric acid, from which it was precipitated by the addition of ammonia. The yield of pure 6-amino-1-hydrindone was 80 per cent. of the theoretical.

(iv) *Reduction of 6-nitro-1-hydrindoxime.* The oxime may be reduced to the amino-ketone by zinc dust and acetic acid, but the reduction is best effected by suspending the oxime (1 gram) in 20 per cent. hydrochloric acid in which tin (2 grams) is allowed to dissolve, the base being isolated as in the experiments described above.

6-Amino-1-hydrindone crystallises from water in deep yellow, flattened needles, and from ethyl alcohol in leaflets melting at 171° . It is readily soluble in hot water or alcohol, but only sparingly soluble in cold water or ether. Dilute solutions in ether and in alcohol show a marked green fluorescence (Found: C = 72.9; H = 6.2; N = 9.6. C_9H_9ON requires C = 73.4; H = 6.1; N = 9.5 per cent.).

The *acetyl* derivative was prepared by warming the base (0.3 gram) with acetic anhydride (2 c.c.) until the yellow colour had vanished and a clear solution was obtained. On cooling, this deposited crystals of the acetyl compound, which was collected and purified by crystallisation from water. It separated in small, colourless leaflets, m. p. 178° , which aggregated to nodular masses (Found: C = 69.9; H = 6.0. $C_{11}H_{11}O_2N$ requires C = 69.8; H = 5.9 per cent.).

The *semicarbazone* of the aminohydrindone was prepared by mixing an alcoholic solution of the ketone with an aqueous solution of semicarbazide acetate. After half an hour, the precipitate was collected and crystallised from boiling aniline, from which small, colourless flakes separated on cooling. The semicarbazone is insoluble in the usual organic solvents, and on heating decomposes, having no definite melting point (Found: N = 27.2. $C_{10}H_{12}ON_4$ requires N = 27.4 per cent.).

6-Acetylmino-1-hydrindoxime (XLVI).—The acetylmino-ketone (3 grams) was dissolved in ethyl alcohol (20 c.c.) and the solution mixed with aqueous hydroxylamine hydrochloride (1.5 grams in 4 c.c. of water) and then with 12 c.c. of 2N-sodium carbonate solution. The next day the crystals which had separated (27 grams) were collected, and the filtrate was evaporated to dryness. The residue, having been washed with a small amount of water to dissolve out the inorganic salts, yielded a further 0.4 gram of the oxime, the total yield amounting to 3.1 grams, that is 96 per cent. of the theoretical.

The oxime is sparingly soluble in water, alcohol, ethyl acetate, or acetone, but dissolves readily in hot glacial acetic acid, from which it separates on cooling in small, colourless prisms, m. p. $225-228^{\circ}$ (decomp.) (Found: C = 64.9; H = 6.2. $C_{11}H_{12}O_2N_2$ requires C = 64.7; H = 5.9 per cent.).

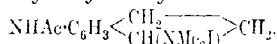
6-Acetylmino-1-hydrindoxime (XLVII).—The oxime (20 grams) was dissolved in 200 c.c. of hot glacial acetic acid, and the solution mixed with 200 c.c. of hot water and treated with 15 kilos. of 4 per cent. sodium amalgam, which was added in such a way that the heat developed during the reduction maintained the temperature. When the reaction was completed, the mercury was separated and

washed with water, and the combined aqueous solutions diluted to 1 litre, nearly neutralised with concentrated sodium hydroxide, and then cooled to 0°. An excess of sodium hydroxide was added and the solution vigorously shaken for a few minutes to coagulate the precipitate, which was then collected and dissolved in hot water, from which the base crystallised on cooling. A further quantity was obtained in the form of its hydrochloride by extracting the aqueous mother-liquors with ether, and then re-extracting from the ether by means of hydrochloric acid.

The free base crystallises from warm water in colourless, glistening laminae, m. p. 65°, containing two molecules of water of crystallisation (Found: C = 58.3; H = 7.7. $C_{11}H_{14}ON_2 \cdot 2H_2O$ requires C = 58.4; H = 8.0 per cent.). The anhydrous base may be obtained by drying the crystallised substance first for twenty-four hours in an evacuated desiccator, and then to constant weight in the steam-oven. It separates from acetone in stout, pale yellow prisms, m. p. 160°. The hydrochloride of the base crystallises from water in compact, highly refracting, colourless prisms.

The *acetyl* derivative (XLVIII), prepared by the action of acetic anhydride on the anhydrous base, separated from dilute acetic acid in colourless needles, m. p. 225° (Found: C = 67.6; H = 6.98, $C_{13}H_{16}O_2N_2$ requires C = 67.2; H = 6.95 per cent.). It was found to be identical with the substance prepared from hydrindamine by nitration, followed by reduction and subsequent acetylation (p. 1485).

6-Acetylamino-1-hydrindyltrimethylammonium Iodide,



—A solution of 5.7 grams of 6-acetylaminohydrindamine in 10 c.c. of methyl alcohol was treated successively with 3.4 grams of potassium hydroxide dissolved in 100 c.c. of methyl alcohol, and with 6 c.c. of methyl iodide. A vigorous reaction ensued, during the course of which potassium iodide separated, and after five minutes the solution was filtered. The filtrate gradually deposited crystals of the quaternary iodide, a further quantity of which was recovered from the mother-liquors by fractionally crystallising from methyl alcohol the residue obtained on evaporation. The iodide separates from methyl alcohol in colourless prisms, m. p. 201° (Found: I = 34.9. $C_{14}H_{18}ON_2I$ requires I = 35.3 per cent.).

The quaternary *hydroxide* is not produced by the action of aqueous alkalis on the iodide, and it is necessary to use silver oxide. On heating, this substance appears to give a small yield of the *acetylaminoindene* (m. p. 135°), but by far the greater portion is converted into substances of high molecular weight which have not yet been closely examined.

6-Hydroxy-1-hydrindone (LXV).—This substance was prepared by diazotising 6-amino-1-hydrindone, dissolved in 2.5 equivalents of 2*N*-sulphuric acid, with the theoretical quantity of sodium nitrite solution, and heating the product at 100° until nitrogen ceased to be evolved. The solution, which while still hot was filtered from the chocolate-coloured precipitate which had formed, on cooling deposited a portion of the hydroxy-ketone, and the remainder was extracted with ether. It was purified by recrystallisation from water, from which it separated in rosettes of slender, yellow needles, melting at 151–153° (Found: C = 72.5; H = 5.3. $C_{11}H_9O_2$ requires C = 72.9; H = 5.4 per cent.). It gives a violet colour with aqueous alcoholic ferric chloride.

When preparing large quantities of this substance, it is unnecessary to isolate either pure 6-nitrohydrindone or pure 6-amino-hydrindone. The crude mononitration product of 1-hydrindone is reduced, and the double tin salt of the base collected and diazotised. One crystallisation from alcohol is sufficient to purify the hydroxy-ketone, 22 grams of which may thus be very quickly obtained from 100 grams of 1-hydrindone.

6-Methoxy-1-hydrindone (LXVI).—The hydroxy-ketone (22 grams) was dissolved in 200 c.c. of 2*N*-sodium hydroxide and treated with four successive portions, each of 5 c.c., of methyl sulphate, the mixture being vigorously agitated after each addition. The liquid quickly became filled with yellow leaflets of the methoxy-compound, which was collected after cooling to 0°, and crystallised from 95 per cent. alcohol, from which it separated in bright yellow, glistening laminae, m. p. 109°. The yield was 21 grams, that is, 80 per cent. of the theoretical (Found: C = 74.16; H = 6.29. $C_{16}H_{16}O_2$ requires C = 74.04; H = 6.22 per cent.).

6-Methoxy-1-hydrindoxime (LXVII).—The ketone (5 grams) dissolved in alcohol (10 c.c.), was treated with a solution of hydroxylamine hydrochloride (4 grams) in 5 c.c. of 90 per cent. alcohol and to the hot solution 8 c.c. of 40 per cent. potassium hydroxide were added. The oxime, which separated at first as an oil, was caused to solidify by shaking, and, after cooling, was collected, washed, and crystallised from alcohol, from which it separated in long, pale yellow needles, m. p. 133° (Found: C = 67.35; H = 6.33. $C_{16}H_{17}O_2N$ requires C = 67.75; H = 6.26 per cent.).

A remarkably stable *molecular compound*, containing one molecule of the ketone and one of its oxime, was obtained when the ketone was treated with 1.5 molecules of hydroxylamine hydrochloride and excess of sodium carbonate according to the usual method of preparing oximes. This substance separated from alcohol in bright yellow needles, m. p. 90° (Found: C = 70.73; H = 6.33).

$C_{20}H_{21}O_4N$ requires $C = 70.90$; $H = 6.24$ per cent.), and did not appear to be capable of resolution into its components by fractional crystallisation from solvents, although treatment with excess of hydroxylamine hydrochloride and boiling alkali converted it into the oxime mentioned above.

6-Methoxy-1-hydrindamine (LXVIII).—The above oxime (6 grams) was dissolved in glacial acetic acid (60 c.c.) and water added until a faint precipitate appeared. Sodium amalgam (3.5 per cent.) was then added at such a rate that the heat developed during the reduction maintained a fairly brisk action. When hydrogen began to be evolved, the reaction was completed by heating, and the mercury then removed. The aqueous liquid was made strongly alkaline at 0° with concentrated potassium hydroxide solution and extracted with ether, the base being re-extracted from the ether with dilute hydrochloric acid. A large proportion of the hydrochloride separated from the acid solution, and the remainder was recovered by evaporation of the mother-liquors in a vacuum.

The *hydrochloride* separates from methyl alcohol in short, colourless prisms, which melt at 250° with sudden decomposition (Found: $Cl = 17.65$. $C_{10}H_{14}ONCl$ requires $Cl = 17.7$ per cent.).

The *acetyl* derivative, which is precipitated when an aqueous solution of the hydrochloride is made strongly alkaline and shaken with acetic anhydride, crystallises from water containing a little alcohol in long, slender needles, m. p. 130° (Found: $C = 69.81$; $H = 7.44$. $C_{12}H_{15}ON$ requires $C = 70.20$; $H = 7.37$ per cent.).

The *molecular* compound (m. p. 77°) of 6-nitrohydrindone and 4-nitrohydrindone, which occurs along with 6-nitrohydrindone in the crude nitration product of 1-hydrindone (p. 1485), separates from light petroleum, ethyl alcohol, or ethyl acetate in colourless prisms, m. p. 77° (Found: $C = 60.9$; $H = 4.2$. $C_9H_7O_5N$ requires $C = 61.0$; $H = 4.0$ per cent.). Its solubility generally resembles that of 6-nitrohydrindone, but it is more soluble in most solvents, the difference being most marked in the case of light petroleum. Like the 6-nitro-compound, its solubility in water is not increased by the addition of sodium carbonate or sodium hydroxide, although after a time the production of tarry material begins to be appreciable. It does not give a coloration with aqueous alcoholic ferric chloride. With acids, it reacts similarly to the 6-nitro-compound, but is noticeably more stable; for instance, it may be heated at 185° with 1 per cent. phosphoric acid for twenty minutes—treatment which completely converts the 6-nitro-compound into insoluble substances and carbonaceous material. Its remarkable stability is shown by the following experiments:

(a) Examination under the microscope showed that it was crystallographically homogeneous, and quite different in appearance and crystalline form (prisms) from the 6-nitroketone (thin laminæ).

(b) On successive fractional crystallisation from light petroleum, ethyl alcohol, and ethyl acetate, these solvents being taken in any order, the melting point remained quite sharp and showed no tendency to change from its original value (77°). Although this melting point is near that of 6-nitrohydrindone (74°), a small amount of either ketone added to a preparation of the other caused a marked depression of melting point, and a mixture of about equal quantities of the two melted at $55-58^{\circ}$.

(c) A considerable bulk of the pure ketone (m. p. 77°) was fused and allowed gradually to solidify, the crystals being separated from time to time in such a way as to divide the whole material into a number of fractions of comparable size. Each of these, as well as mixtures of them, melted sharply at 77° .

Admixture with 6-nitrohydrindone depressed the melting point, but not with the original specimen of the molecular compound itself.

(d) The oxime (below), which was formed in almost quantitative yield, and melted, before recrystallisation, at $179-181^{\circ}$ (when quite pure, it melts at 181°), depressed the melting point of the oxime of the 6-nitroketone, and on hydrolysis with mineral acids gave back the original ketone, which, without recrystallisation, melted at $76-77^{\circ}$, and was identified as the molecular compound (m. p. 77°) by a mixed melting point determination.

(e) The semicarbazone (below) was crystallised from glacial acetic acid, in which the semicarbazone of 6-nitrohydrindone is almost insoluble. No trace of any less soluble semicarbazone could be detected, and the crystallised substance on hydrolysis by acids yielded the ketone, m. p. 77° , in the pure condition.

(f) The oxime was separated into four fractions, all melting between 179° and 181° , by crystallisation from ethyl acetate. The ketone was regenerated from each of these separately, and the substances obtained from the first and third fractions of the oxime further subdivided by fractional crystallisation from alcohol. Every fraction, and all mixtures of them, melted at 77° or $76-77^{\circ}$ and showed no depression of melting point when mixed with a specimen from the stock of the original ketone, but, on the other hand, gave a marked depression with 6-nitrohydrindone.

(g) The ketone (m. p. 77°) was treated with enough semicarbazide acetate to combine with half of it. The unchanged ketone was separated from the semicarbazone with the help of chloroform (this operation was quantitative, the semicarbazone being quite insoluble), and was identified as the pure ketone (m. p.

77°). The semicarbazone was then hydrolysed with hydrochloric acid, and the recovered ketone identified as the same pure ketone (m. p. 77°). Both specimens melted sharply, alone or in admixture.

(h) A similar experiment on oxime formation, using half an equivalent of hydroxylamine, gave a precisely similar result.

The oxime was prepared like that of 6-nitrohydrindone (p. 1486), and purified by crystallisation from ethyl acetate, from which it separated in long, colourless needles, m. p. 181° (Found: C = 56.0; H = 4.6. $C_9H_8O_3N_2$ requires C = 56.2; H = 4.2 per cent.). It rapidly dissolves in boiling 10 per cent. hydrochloric acid, from which part of the regenerated ketone separates as an oil while still hot, and the remainder in the crystalline form on cooling. It may be collected by filtration, or extracted with chloroform.

The semicarbazone was prepared like that of 6-nitrohydrindone, and crystallised from glacial acetic acid, from which it separated in short, hard prisms, which on heating decomposed (Found: C = 51.4; H = 4.6. $C_{10}H_{10}O_3N_4$ requires C = 51.3; H = 4.3 per cent.).

The regeneration of the ketone was accomplished as in the instance previously described (p. 1487).

The *p*-nitrophenylhydrazone was obtained by allowing the ketone to react with *p*-nitrophenylhydrazine in boiling alcoholic solution for three minutes. After cooling, the hydrazone slowly crystallised in rosettes of small, yellow needles, which decomposed on heating above 200°. It was too insoluble in the usual solvents to be recrystallised conveniently.

2:2-Dibromo-4-nitro-1-hydrindone (L).—Four grams of the ketone, m. p. 77°, were dissolved in chloroform at 9° and titrated with a 25 per cent. solution of bromine in chloroform until immediate decoloration ceased. The quantity of bromine absorbed corresponded with 4.15 atoms. The solid which remained after the chloroform had been evaporated was dissolved in hot ethyl acetate (10 c.c.) and allowed to crystallise until about one-fourth had been deposited. This was collected and again crystallised (Found: Br = 47.7. $C_9H_5O_3NBr_2$ requires Br = 47.7 per cent.).

2:2-Dibromo-4-nitro-1-hydrindone separates from alcohol or ethyl acetate in long, thin blades, which melt at 140°. It is considerably less soluble in organic solvents than its 6-nitro-isomeride (m. p. 112°), which may be isolated from the mother-liquors obtained on crystallising the crude bromination product. On oxidation with alkaline permanganate, it gives 3-nitrophthalic acid. Aqueous sodium iodide acidified with acetic acid does not reduce it, but by means of stannous chloride and hydrochloric acid the amino-ketone can be obtained (below). It was not found possible to obtain 4-nitro-1-hydrindone by partial reduction of the bromonitro-ketone

4-Amino-1-hydrindone (LII).—This substance has been prepared in the following ways:

(i) *Reduction of the crude nitration product of 1-hydrindone.* The manner of conducting this experiment has already been described (p. 1488). The 4-amino-ketone was isolated from the more soluble portion of the base obtained from the ether extract, and was purified by crystallisation from ether. The separation of the last trace of the 6-amino-ketone was attended with some difficulty.

(ii) *Reduction of the molecular compound, m. p. 77°.* This reduction was conducted like the previous one and the products were separated in the same way. The yield of the 6-amino-ketone was about 40 per cent., and a comparable quantity of the 4-amino-ketone appeared to be present, although it could not all be separated in the pure condition.

(iii) *Reduction of 2:2-dibromo-4-nitro-1-hydrindone.* This experiment was carried out like the reduction of the 2:2-dibromo-6-nitro-ketone (p. 1489), excepting that it was found advisable, owing to the instability of the 4-amino-ketone, to isolate the double tin salt by evaporating the solution to small bulk after the reduction had been completed. This was then decomposed by sodium hydroxide, and the precipitated base collected (0.4 gram from 1.8 grams of dibromo-ketone), a further quantity being obtained by working up the alkaline mother-liquors and the filtrate from the tin salt as described on p. 1489. The 4-amino-ketone was isolated in the pure condition by crystallisation from hot water.

(iv) *Reduction of the oxime of the ketone, m. p. 77°.* This reduction was carried out like the one described on p. 1489, the products being separated as indicated above.

4-Amino-1-hydrindone crystallises from water in thin, very pale yellow laminae melting at 125°. It is moderately soluble in water, ether, alcohol, or benzene, from any of which it can conveniently be crystallised (Found: C = 73.5; H = 6.2. C_9H_9ON requires C = 73.4; H = 6.1 per cent.). An attempt to prepare the corresponding hydroxyhydrindone by diazotisation led to the production of tarry substances.

The *acetyl* derivative, prepared like the isomeric acetyl derivative mentioned on p. 1490, separated from alcohol in minute, colourless needles, which melted at 143–145°. It is more soluble in water or alcohol than the isomeride of melting point 178°.

(B) Orientation of 4- and 6-Substituted Hydrindamines and Hydrindones.

Hydrindone may be oxidised by means of alkaline permanganate to phthalic acid, but by using chromic acid under carefully regulated

conditions homophthalic acid may be made to become the principal product. The method is a very convenient one for preparing this acid in quantity.

Homophthalic Acid (XXXVIII).—The 1-hydrindone (18 grams) was added to 800 c.c. of a boiling solution of chromic acid, made by dissolving 300 grams of chromium trioxide and 250 c.c. of concentrated sulphuric acid in 3000 c.c. of water. Reduction of the chromic acid took place at once and the heat developed kept the liquid boiling vigorously for about two minutes, during which the flask was continuously shaken. Heat was applied for a further two minutes, and the solution was then allowed to cool. After the homophthalic acid which had crystallised (12 grams) had been separated, the liquid was extracted with ether and the acid removed from the extract by shaking with a small amount of concentrated aqueous sodium hydroxide, from which, on subsequent acidification, a further quantity crystallised (5 grams). Re-extracting the mother-liquors with ether yielded a further 2 grams. Crystallisation of the combined crops from hot water gave 17 grams of pure homophthalic acid and a small amount (less than 1 gram) of phthalic acid.

4-Nitrohomophthalic acid (XL).—This substance was obtained by direct nitration of homophthalic acid, by oxidation of the nitrohydrindones, and by oxidation of 6-nitro-1:2-diketo-hydrindene.

(i) *Nitration of homophthalic acid*. Two grams of homophthalic acid were dissolved in 16 grams of fuming nitric acid (*d* 1.5) at the ordinary temperature. After keeping for two hours, the solution was diluted with an equal bulk of water and allowed to crystallise. The solid which separated was collected, and was found to consist of pure 4-nitrohomophthalic acid (Found: C = 48.0; H = 3.2. Calc., C = 48.0; H = 3.1 per cent.).

(ii) *Oxidation of 6-nitrohydrindone*. (a) The ketone (1.5 grams) was added to 60 c.c. of a solution of chromic acid, made by dissolving 20 grams of potassium dichromate and 18 c.c. of concentrated sulphuric acid in 100 c.c. of water. The whole was heated over a free flame until the ketone had completely disappeared and then on a steam-bath for thirty minutes. The cooled solution was shaken with ether, and the acid products were extracted from the ether with aqueous sodium carbonate. On adding hydrochloric acid, almost the whole of the 4-nitrohomophthalic acid was precipitated (0.82 gram), whilst the 4-nitrophthalic acid (0.8 gram) remained in solution (see below).

(b) In another experiment the ketone (2 grams) was boiled for five minutes with 50 c.c. of a solution of chromic acid prepared

by dissolving 30 grams of chromium trioxide and 25 c.c. of sulphuric acid in 300 c.c. of water. Most of the nitrohomophthalic acid crystallised on cooling, but a further quantity was isolated by extracting with ether as described above. The yield was 1.5 grams, that is, about 60 per cent. of the theoretical. The soluble acids were not investigated in this particular experiment. The nitrohomophthalic acid was identified with that obtained as the main nitration product of homophthalic acid by analysis (Found: C = 47.9; H = 3.2. Calc., C = 48.0; H = 3.1 per cent.), and by a mixed melting point determination both of the acid and its methyl ester (below).

(iii) *Oxidation of the nitrohydrindone, m. p. 77°.* (a) On oxidation by method (a) (above), 1.5 grams of this ketone gave 0.6 gram of 4-nitrohomophthalic acid.

(b) * On oxidation by a process essentially the same as method (b) (above), 10 grams of the ketone gave 4 grams of nitrohomophthalic acid and some amorphous products. The nitrohomophthalic acid was identified by analysis (Found: C = 48.0; H = 3.2. Calc., C = 48.0; H = 3.1 per cent.), and by direct comparisons and mixed melting point determinations of the acid itself and its methyl ester with the specimens of those substances obtained by the methods described above.

(iv) *Oxidation of 6-nitro-1:2-diketohydrindone.* Ten c.c. of a solution of chromic acid, prepared by dissolving 30 grams of chromium trioxide and 25 c.c. of concentrated sulphuric acid in 500 c.c. of water, were warmed to 70° and the diketone (0.57 gram) was added. It immediately dissolved with reduction of the chromic acid. After five minutes, the solution was filtered from a small, amorphous residue, cooled to 0°, and kept at that temperature for three hours, after which the nitrohomophthalic acid was collected. A further small amount was obtained by extracting the mother-

* A small amount of another acid was isolated from the ultimate residue obtained in this and some similar experiments. This substance, on analysis, gave figures corresponding with the formula $C_{11}H_5O_5N$ (Found: C = 44.8; H = 3.0; N = 5.9. $C_{11}H_5O_5N$ requires C = 44.8; H = 2.9; N = 5.9 per cent.). It forms white, rhombic crystals, which separate readily from water or from a mixture of ether and chloroform, and melt at 161–162°. It is remarkably stable towards alkaline permanganate and we have not yet succeeded in obtaining a recognisable oxidation product. It does not give a coloration with ferric chloride, and, although titration shows quite definitely that it is a dibasic acid, it appears to have no appreciable tendency to lose water when heated at 100°. We do not at present feel able to offer any definite suggestion as to the structure of this substance and have had to postpone a more detailed examination of its properties until a further large quantity of material is available, as the amount of the acid formed by oxidation is very small.

liquors with ether, the total yield being 0.45 gram. The acid was identified with the same substance obtained by other methods as in the previous experiment. Attempts which were made to oxidise the diketone by means of hydrogen peroxide were unsuccessful.

4-Nitrohomophthalic acid is moderately soluble in hot water, but only very sparingly soluble in cold. It crystallises from water in prismatic needles which melt with decomposition at 220°. On oxidation by means of hot alkaline permanganate, it yields 4-nitrophthalic acid.

The Methyl Ester.—All specimens of 4-nitrohomophthalic acid were converted into methyl 4-nitrohomophthalate to confirm their identity, the process usually employed being as follows. The acid (0.3 gram) was warmed with 1 gram of phosphorus pentachloride until hydrogen chloride ceased to be evolved, and the product, after cooling, was treated with 3 c.c. of methyl alcohol. The methyl-alcoholic solution was concentrated by boiling and diluted with water, and the oil thereby precipitated, which adhered to the walls of the tube, was washed with water by decantation and rubbed with dilute aqueous sodium carbonate until it had completely solidified. The solid ester was then collected, washed with water, dried, and crystallised from dry ether, from which it separated in small tablets melting at 92.5° (Found: C = 51.8; H = 4.6. $C_{11}H_{11}O_4N$ requires C = 52.1; H = 4.4 per cent.).

4-Nitrophthalic Acid (XXXIX).—This acid was obtained by oxidising 6-nitrohydrindone with chromic acid or permanganate, and by oxidising the 2:2-dibromo-6-nitro-1-hydrindone and 4-nitrohomophthalic acid by alkaline permanganate.

(i) *Oxidation of 6-nitro-1-hydrindone by chromic acid.* The aqueous solution of 4-nitrophthalic acid which was obtained in experiment (ii, a) described on p. 1497, was extracted repeatedly with ether, and the extract dried and evaporated. The residue solidified after a short time, and was then crystallised from a mixture of ether and chloroform. The acid was identified by its melting point (164°), by analysis (Found: C = 45.6; H = 2.6. Calc., C = 45.5; H = 2.4 per cent.), and by the melting point and properties of its characteristic aniline salt (m. p. 181°). These agreed in all particulars with the description given in the literature.

(ii) *Oxidation of 6-nitro-1-hydrindone by alkaline permanganate.* The ketone (1 gram) was suspended in 10 c.c. of 2N-sodium hydroxide solution, and the whole stirred vigorously with a mechanical agitator while 3 per cent. potassium permanganate was slowly run in until the pink colour persisted. The amount of permanganate used corresponded with about five atoms of available oxygen. The mixture was filtered and the precipitate twice suspended in water

and treated with a current of steam. The combined filtrates were acidified with hydrochloric acid and evaporated to a pasty mass, which was extracted with a large amount of ether. The acid products were separated by extraction from the ether with sodium carbonate, and recovered from the alkaline solution by re-extracting with ether after acidification. The main product was 4-nitrophthalic acid, which occurred to the extent of about 40 per cent. of the amount theoretically possible, together with a small quantity of a solid, amorphous material, some tar, and some gum. The nitrophthalic acid was identified as in the previous experiment. No trace of nitrohomophthalic acid could be detected.

The oxidation may also be carried out in the presence of sodium carbonate instead of the hydroxide, but the reaction is much slower in this case. The main product is, however, as before, 4-nitrophthalic acid, unaccompanied by any trace of 4-nitrohomophthalic acid. The reaction is extremely sluggish if an excess of magnesium sulphate is present, and it is a difficult matter to bring about the absorption of more than three atoms of oxygen. Even in this case, however, no 4-nitrohomophthalic acid is formed, the only crystalline product being 4-nitrophthalic acid.

(iii) *Oxidation of the nitrohydrindone, m. p. 77°, by chromic acid.* The 4-nitrophthalic acid was isolated from experiment (iii, a) (p. 1493) as in the experiment (i) described above on the oxidation of the 6-nitro-ketone. The product was identified in the same way.

(iv) *Oxidation of the nitrohydrindone, m. p. 77°, by alkaline permanganate.* This experiment was conducted like experiment (ii) above. The results obtained were exactly similar.

(v) *Oxidation of 2:2-dibromo-6-nitro-1-hydrindone.* The bromo-ketone (2 grams) was finely powdered and kept in suspension in 10 c.c. of 2*N*-aqueous sodium hydroxide by mechanical agitation while 3 per cent. permanganate was added to keep pace with decoloration. The reaction was very slow and after four hours only 2.1 atoms of oxygen had been used. The acid oxidation products were isolated as in experiment (i) (above), and were thus obtained as a viscous gum, from which, on adding a little aniline and 1 c.c. of ethyl alcohol, the aniline salt of 4-nitrophthalic acid separated. This was recrystallised from hot alcohol and the free acid regenerated from it. It was identified by direct comparison and by mixed melting-point determinations.

(v) *Oxidation of 4-nitrohomophthalic acid.* The nitrohomophthalic acid (0.5 gram) was dissolved in 3 c.c. of 2*N*-sodium carbonate solution and boiled with 0.65 gram of potassium permanganate, dissolved in 6 c.c. of water, for an hour, when the colourless solution

was filtered and the precipitate treated with steam in the usual manner. The acid was isolated from the filtrates by extraction with ether after acidifying and concentrating, and was purified by crystallisation from a mixture of ether and chloroform. It was identified by direct comparison and by mixed melting-point determinations with previously obtained specimens, and by conversion into its characteristic aniline salt.

3-Nitrophthalic Acid (LI).—This substance was obtained by oxidising 2:2-dibromo-4-nitro-1-hydrindone with alkaline permanganate. The bromo-ketone (0.95 gram) was finely ground and suspended in 10 c.c. of a 2*N*-solution of sodium hydroxide to which 10 c.c. of water was added. The liquid was stirred by a mechanical agitator while a total of 33 c.c. of permanganate solution (equivalent to 3 atoms of oxygen) was added. The reaction proceeded somewhat slowly, with intermediate formation of manganate, and had to be completed by warming. The acid product, isolated in the usual way, proved to be 3-nitrophthalic acid. Its identity was proved by analysis (Found: $C = 45.2$; $H = 2.6$. Calc., $C = 45.5$; $H = 2.4$ per cent.), and by the melting point of its mixture with an authentic specimen. The yield was 0.32 gram, that is, 54 per cent. of the theoretical.

(C) 5- and 7-Substitution Products of Hydrindamine and Hydrindone.

***m*-Nitrocinnamic Acid (LIII).**—This was prepared by the condensation of *m*-nitrobenzaldehyde with sodium acetate and acetic anhydride, following the method employed by Schiff (*Ber.*, 1878, 11, 1782). The acid thus obtained formed almost colourless needles, m. p. 196°.

***m*-Aminocinnamic Acid (LIV).**—This substance has been prepared by Tiemann and Oppermann (*Ber.*, 1880, 13, 2064) by the reduction of the nitro-acid with ferrous sulphate and barium hydroxide or with stannous chloride. The hydrochloride was decomposed with sodium acetate (Gabriel, *Ber.*, 1882, 16, 2038), or with the theoretical quantity of sodium carbonate. Crystallised from alcohol, the amino-acid forms bright yellow needles, m. p. 185° (Found: $C = 65.97$; $H = 5.66$. Calc., $C = 66.23$; $H = 5.56$ per cent.).

The acetyl derivative, which was made by the action of acetic anhydride on the amino-acid, crystallised from dilute acetic acid in minute, colourless prisms, m. p. 237° (Found: $C = 64.44$; $H = 5.54$. $C_{11}H_{11}O_3N$ requires $C = 64.32$; $H = 5.40$ per cent.).

***m*-Hydroxycinnamic Acid (LV).**—For the preparation of the hydroxy-acid (compare Gabriel, *Ber.*, 1882, 15, 2297), isolation of the free amino-acid is unnecessary. A yield of 50–60 per cent. may be obtained directly from the nitro-acid as follows: *m*-Nitro-

cinnamic acid (70 grams) was added to a solution of 340 grams of stannous chloride ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$) in 400 c.c. of hydrochloric acid. The acid dissolved with the evolution of much heat, and with rapidly increasing velocity, the reaction finally becoming very violent. The clear solution, on cooling, deposited a mass of colourless prisms of the tin double salt of *m*-aminocinnamic acid, which were removed, washed with a little dilute hydrochloric acid, dissolved in a litre of water to which 500 c.c. of 2*N*-sulphuric acid had been added, and the solution, cooled in ice, was treated with a solution of 35 grams of sodium nitrite. The addition having been completed, the liquid was slowly heated to, and kept at boiling temperature until nitrogen ceased to be evolved. The boiling solution, which was filtered from the precipitated stannic hydroxide and tarry matters, on cooling, deposited the hydroxy-acid in an almost pure condition. (Without further purification, it melted at $185\text{--}189^\circ$, and was of sufficient purity for methylation.) On recrystallisation from hot water, it was obtained as pale buff prisms, *m. p.* 191 (Found: $\text{C} = 65.78$; $\text{H} = 5.12$. Calc., $\text{C} = 65.63$; $\text{H} = 4.91$ per cent.).

m-Methoxycinnamic acid (LV1) is obtained by methylation of the hydroxy-acid. Methyl iodide in alkaline solution gives the methyl ester (Tiemann and Ludwig, *Ber.*, 1882, **15**, 2951), hence the methylation was effected with methyl sulphate. The acid (100 grams) was dissolved in 400 c.c. of 2*N*-aqueous sodium carbonate, and methyl sulphate (100 c.c.) added in portions of 10 c.c. with vigorous agitation. When the methyl sulphate had completely dissolved, the solution was heated to boiling and kept at boiling temperature until the odour of methyl sulphate had disappeared. It was then cooled, neutralised, and a small excess of hydrochloric acid added. The solution was freed from the gummy matter thus precipitated, and treated with a large excess of hydrochloric acid. The methoxy-acid was thus obtained as a white, crystalline powder, *m. p.* $105\text{--}109$. A sample recrystallised from water melted at $113\text{--}114$ (Tiemann and Ludwig give the melting point as 111).

m-Methoxy- β -phenylpropionic acid (LVH) was prepared by Tiemann and Ludwig by the reduction of the above acid. Their method was followed in all respects save in the isolation and purification, as it was found that by cooling the alkaline solution after reduction and careful addition of cold, 20 per cent. hydrochloric acid, the acid was obtained as a white, crystalline precipitate, which, on drying in ether and crystallising from a mixture of ether and ligroin, formed clusters of colourless laminae, *m. p.* 45° (Tiemann and Ludwig give the *m. p.* of their crude acid, after

pressing between filter-paper, as 51° , and state that it was too soluble in the common organic solvents to be crystallised therefrom).

m-Methoxy- β -phenylpropionyl chloride (LVIII) was obtained when the acid was warmed with an equal weight of thionyl chloride until the evolution of hydrogen chloride and sulphur dioxide ceased. The excess of thionyl chloride was removed by heating to 100° in a vacuum. The bulk of the residue distilled at $165^{\circ}/22$ mm., leaving a tarry residue, and was obtained in a pure condition by a second distillation. It is a light yellow oil which rapidly darkens on exposure to air and light. On heating with water, it is hydrolysed to the acid (Found: Cl = 17.8. $C_{10}H_{11}O_2Cl$ requires Cl = 17.9 per cent.).

Action of Aluminium Chloride on Methoxyphenylpropionyl Chloride.—The chloride (15 grams), dissolved in 30 c.c. of dry petroleum (b. p. $70-80^{\circ}$), was treated with 15 grams of finely powdered aluminium chloride. The violent reaction, which was accompanied by the evolution of much hydrogen chloride, was completed by heating on the steam-bath for a few minutes, and the deep red, viscous substance thus obtained was collected and decomposed by ice and water. The colourless, crystalline solid produced was removed and crystallised from methyl alcohol.

5-Methoxy-1-hydrindone (LIX).—This substance separates from methyl or ethyl alcohol in colourless prisms, m. p. 110° . It is readily soluble in the usual organic solvents, excepting ether and light petroleum, and is fairly soluble in hot water, from which it crystallises in silky needles (Found: C = 73.96; H = 6.32. $C_{10}H_{10}O_2$ requires C = 74.04; H = 6.22 per cent.).

The *semicarbazone*, which is obtained when an aqueous solution of the ketone is treated with semicarbazide, separates from dilute acetic acid in colourless, glistening leaflets, m. p. 239° .

5-Hydroxy-1-hydrindone (LXI).—This substance and its isomeride, 7-hydroxy-1-hydrindone, remained in the aqueous solution from which the methoxy-ketone was precipitated after the aluminium compound had been decomposed by ice and water (above). The two hydroxy-ketones were separated by taking advantage of their difference of volatility.

The aqueous solution was combined with the aqueous mother-liquors obtained on recrystallising the methoxy-ketone, and the whole evaporated to dryness. The residue was then distilled in a current of steam until the distillate failed to give a coloration with ferric chloride. The residue obtained on evaporating the solution in the distilling flask was boiled with methyl alcohol and animal charcoal, and the filtered solution allowed to crystallise, when pale yellow prisms, m. p. 182° , of the 5-hydroxy-compound separated

(Found: C = 72.75; H = 5.54. Calc., C = 72.94; H = 5.45 per cent.). This hydroxy-ketone gives only a faint red colour with ferric chloride (contrast the 7-hydroxy-ketone). Auwers and Hilliger (*Ber.*, 1916, **49**, 2410) record 183° as the m. p. and state that the yellow colour is due to a trace of some impurity.

On methylation with methyl sulphate and alkali, this hydroxy-ketone gives the methoxy-ketone (above) which forms the main product of the decomposition with aluminium chloride.

7-Hydroxy-1-hydrindone (LXI).—The steam-distillate (above) was saturated with sodium chloride and extracted with ether, and the extract dried and evaporated. The solid residue consisted mainly of the 7-hydroxy-ketone, but it contained in addition a little 5-methoxy-ketone and possibly also some 7-methoxy-ketone. These were removed by grinding with cold 2*N*-aqueous sodium hydroxide and filtering. The 7-hydroxy-ketone was precipitated from the filtrate by means of hydrochloric acid and crystallised from methyl alcohol, from which it separated in colourless, elongated prisms, m. p. 111° (Found: C = 72.93; H = 5.58. Calc., C = 72.94; H = 5.45 per cent.). This ketone gives an intense violet colour with ferric chloride, and its melting point and properties agree with Auwers and Hilliger's description (*loc. cit.*).

5-Methoxy-1-hydrindoxime (LXVIII).—The 5-methoxy-ketone (1 gram), dissolved in 2 c.c. of ethyl alcohol, was treated with a solution of hydroxylamine hydrochloride (0.5 gram) in 1 c.c. of water and 3 c.c. of 2*N*-aqueous sodium carbonate. After keeping at 50–60° for one hour, colourless crystals separated, which were collected, washed with hot water, and crystallised from methyl alcohol. The oxime forms colourless, silky needles, m. p. 151° (Found: C = 67.70; H = 6.32. $C_{10}H_{11}O_2N$ requires C = 67.75; H = 6.26 per cent.).

5-Methoxy-1-hydrindamine (LXVIII). The above oxime was reduced with sodium amalgam and 50 per cent. acetic acid in the same way as its isomeride (compare p. 1493), and the base isolated in the same way excepting that in this case the hydrochloride did not crystallise until most of the solvent had been removed by evaporation in a vacuum.

The *hydrochloride* separates from a mixture of methyl alcohol and ethyl acetate in stellate clusters of colourless prisms, which melt at 230° with the precipitation of ammonium chloride (Found: Cl = 16.9. $C_{10}H_{11}ONCl$ requires Cl = 17.7 per cent.).

The *acetyl* derivative, prepared in the same way as its isomeride (p. 1493), separates from alcohol in minute, colourless prisms, m. p. 135° (Found: C = 69.8; H = 7.39. $C_{12}H_{13}O_2N$ requires C = 70.2; H = 7.37 per cent.).

(D) *Action of Aluminium Chloride on p-Nitrophenylpropionyl Chloride.*

p-Nitro-β-phenylpropionyl Chloride.—*p*-Nitro-β-phenylpropionic acid (10 grams) (prepared by nitrating β-phenylpropionic acid according to Beilstein and Kühlberg's method, *Annalen*, 1872, **163**, 132) was heated with thionyl chloride (8 grams) until hydrogen chloride ceased to be evolved. The excess of thionyl chloride was removed by heating in a vacuum at 100°. The residual oil solidified on cooling, but the substance was too unstable in air for the melting point to be determined accurately by the usual method. The acid chloride was purified for analysis by distillation, but the operation was always attended with the risk of explosion. It passed over at 204°/7 mm. as a colourless oil, which solidified in the receiver (Found: Cl = 16·5. $C_9H_8O_3NCl$ requires Cl = 16·6 per cent.).

p-Nitro-β-phenylpropaldehyde (LXXII).—This substance was formed when an attempt was made to convert the above acid chloride into the 1-hydrindone by the action of aluminium chloride. The solvent employed was thionyl chloride, 120 c.c. of which were allowed to react with *p*-nitro-β-phenylpropionic acid (37·5 grams) until no more hydrogen chloride was evolved. Finely powdered aluminium chloride was then added to the hot solution, and, after the vigorous reaction had subsided (about ten minutes), the whole was heated for a further forty-five minutes and then cooled and poured on ice. The aqueous solution thus obtained was boiled to expel sulphur dioxide and then extracted with much ether, the extract being washed with aqueous sodium carbonate to remove acid products. In this way, about 75 per cent. of the *p*-nitrophenylpropionic acid originally used was recovered. The neutral extract on evaporation gave a solid, which was sparingly soluble in ether and separated from ethyl alcohol in long needles, m. p. 108° (Found: C = 60·3; H = 5·0. $C_9H_8O_3N$ requires C = 60·3; H = 5·0 per cent.). The yield was 15 per cent. of the theoretical. The constitution of the aldehyde was proved by oxidation by 30 per cent. chromic acid (below).

The *oxime* was obtained by warming the aldehyde (0·5 gram), dissolved in 10 c.c. of ethyl alcohol, with a solution of hydroxylamine hydrochloride (0·3 gram) and sodium carbonate (0·2 gram) in 3 c.c. of water. The mixture having been maintained at 70° for half an hour, water was added and the precipitate collected after cooling. The oxime separated from ethyl alcohol as feathery needles, m. p. 130–131°. It was more soluble in alcohol than the original aldehyde.

p-Nitrophenylacetic Acid and p-Nitrobenzoic Acid.—The aldehyde

(1 gram) was warmed with 10 c.c. of a solution of chromic acid, prepared by dissolving chromium trioxide (30 grams), sulphuric acid (25 c.c.), and acetic acid (25 c.c.) in water (50 c.c.). The reaction proceeded with evolution of heat and on adding water two crystalline acids separated. The less soluble proved to be *p*-nitrobenzoic acid (Found: C = 50.7; H = 3.3. Calc., C = 50.3; H = 3.0 per cent.), and the other *p*-nitrophenylacetic acid (Found: C = 52.9; H = 4.2. Calc., C = 53.0; H = 3.9 per cent.). Both acids had the melting points recorded in the literature, and the former was identified by direct comparison with an authentic specimen.

(E) 5(or 6)-Methoxyindene and its Derivatives.

5(or 6)-Methoxyindene (LXIX or LXX).—(a) From 5-Methoxy-1-hydrindamine. The hydrochloride of the base was heated in a small distilling flask, and the distillate, which contained a little ammonium chloride, mixed with dry ether and filtered. After evaporation of the ether, the indene distilled constantly at 236°/768 mm., and was thus obtained in 80 per cent. yield as a colourless liquid, which, however, turned yellow on keeping, even if sealed from the air and placed in the dark (Found: C = 81.76; H = 6.85. $C_{10}H_{10}O$ requires C = 82.14; H = 6.90 per cent.).

(b) From 6-Methoxy-1-hydrindamine. This reaction was carried out in the same way, and the product (Found: C = 81.43; H = 6.94 per cent.) identified with the preceding one by direct comparison and by means of the solid derivatives described below.

The *picrate* separated as a mass of deep red needles when the indene (obtained by either process) and picric acid were mixed in the correct proportions in alcoholic solution. After crystallisation from a small quantity of alcohol, it melted sharply at 64° (Found: N = 11.8. $C_{15}H_{13}O_8N_3$ requires N = 11.2 per cent.).

The *dibromo-additive* product was prepared by mixing a chloroform solution of the indene with chloroform containing the equivalent of two atoms of bromine. The residue obtained on concentration crystallised from alcohol in pearly leaflets, m. p. 100–101° (Found: Br = 52.24. $C_{10}H_8OBr_2$ requires Br = 52.30 per cent.).

(F) Oxidative Fission of the Methoxyindene.

The indene (2.0 grams) was mixed with twice its volume of glacial acetic acid and added in the cold to 200 c.c. of a solution of chromic acid prepared by dissolving 30 grams of chromium trioxide, 25 c.c. of glacial acetic acid, and 25 c.c. of concentrated sulphuric acid in 100 c.c. of water. The mixture was shaken frequently during two hours and then at intervals over a period of four days, after which it

was treated for one hour on the steam-bath, cooled, and filtered. The plastic mass thus obtained was transferred to a mortar and ground with successive small quantities of sodium carbonate solution until no precipitate was obtained on acidification with concentrated hydrochloric acid. The acidified extracts were combined and filtered, and the filtrate was mixed with the chromium solution and extracted with ether.

5-Methoxyhomophthalic Acid (LXXIII).—The acid precipitated on acidification of the sodium carbonate extracts (above) consisted of almost pure 5-methoxyhomophthalic acid. The residue obtained on evaporation of the ether extract consisted of a mixture of crystalline acids, from which 5-methoxyhomophthalic acid was easily isolated by rubbing with a small amount of water and filtering. The acid crystallises from hot dilute acetic acid in well-defined needles which melt and evolve water vapour at about 222° , the exact temperature depending on the rate of heating. Using the bulb-form of apparatus, apparent melting points as low as 218° and as high as 227° may be obtained by varying the rate of heating within fairly wide limits (Found: C = 56.8; H = 4.8. $C_{10}H_{10}O_5$ requires C = 57.1; H = 4.8 per cent.).

4-Methoxyphthalic Acid (LXXV).—This acid, along with another easily soluble acid which was not identified, dissolved in the water with which the residue from the ether extract was triturated. It was obtained in the pure condition by crystallisation from a small quantity of water, and then melted at 163° (Fritsch gives m.p. 164° , —*Annalen*, 1897, 296, 359) (Found: C = 53.0; H = 3.9. Calc., C = 53.1; H = 4.1 per cent.).

Orientation of 5-Methoxyhomophthalic Acid.—The orientation of this acid is established by the fact that it is the main product of the action of boiling chromic acid on 5-methoxy-1-hydrindone. The ketone (1 gram) was added to 40 c.c. of a solution of chromic acid made by dissolving 10 grams of chromium trioxide and 10 c.c. of concentrated sulphuric acid in 100 c.c. of water. The reaction was started by heating to the boiling point, and then allowed to proceed without the application of heat. When its violence had abated, the mixture was heated on the steam-bath for one hour and then cooled. A considerable quantity of the methoxyhomophthalic acid separated and was collected. The filtrate on extraction with ether gave a mixture of 5-methoxyhomophthalic acid and 4-methoxyphthalic acid, which were separated by triturating with water in the manner described above. The yield of 5-methoxyhomophthalic acid amounted to 70 per cent., and of 4-methoxyphthalic acid to 15 per cent., of the theoretical.

(G) *Alkylidene Derivatives of the Methoxyindene.*

5(or 6)-*Methoxy-1-benzylidene-3- α -hydroxybenzylidene* (LXXVIII or LXXIX).—A mixture of 1.5 grams of the methoxyindene and 1.1 grams of pure benzaldehyde was added to a well cooled solution of sodium ethoxide, prepared by dissolving 0.23 gram of sodium in 3 grams of ethyl alcohol. The crystals, which began to separate after about three hours, were collected after twenty-four hours, washed with water and a little alcohol, and finally crystallised from boiling alcohol, from which the pure benzylidene compound separated in silky, lemon-yellow needles, m. p. 128° (Found: C = 84.8; H = 6.1. $C_{17}H_{14}O$ requires C = 84.7; H = 5.9 per cent.).

The mother-liquors from which this substance separated contained another compound, which was not isolated in a pure condition. After many crystallisations, a specimen, m. p. 111 – 116° , was obtained which on admixture with a little of the substance melting at 128° , melted at 96 – 104° . Analysis of the impure specimen indicated that it consisted essentially of a benzylidene compound isomeric with the substance having m. p. 128° .

5(or 6)-*Methoxy-1-piperonylideneindene* (LXXX or LXXXI).—*Lemon-yellow isomeride*. When a mixture of 1.46 grams of the indene with 1.5 grams of piperonal was added to a solution of sodium ethoxide prepared from 0.23 gram of sodium and 4 grams of alcohol, a second layer separated out almost immediately below the alcoholic solution and rapidly became deep yellow and very viscous. After twenty-four hours, it was washed with ethyl alcohol by decantation and then caused to solidify by rubbing with benzene. The solid product was fractionally crystallised from benzene, and then from various mixtures of benzene and alcohol, and it was thus separated into a mixture of sparingly soluble substances, m. p. 160 – 180° , of the composition $C_{26}H_{20}O_6$, together with two pure compounds, a less soluble, lemon-yellow substance, and a more soluble, orange-yellow compound. The lemon-yellow compound separated from benzene in silky needles, m. p. 148° (Found: C = 77.4; H = 5.1. $C_{18}H_{14}O_3$ requires C = 77.7; H = 5.0 per cent.). *Orange-yellow isomeride*. The orange-yellow compound was obtained in a pure condition after several crystallisations from mixtures of benzene and alcohol, from which it separated in dense, orange-yellow prisms, m. p. 142° (Found: C = 77.2; H = 5.0. $C_{18}H_{14}O_3$ requires C = 77.7; H = 5.0 per cent.). A mixture of the two isomerides melted at 128 – 131° .

5(or 6)-*Methoxy-1-piperonylidene-3- α -hydroxypiperonylidene* (LXXXII or LXXXIII). After a considerable number of crystallisations, one of the constituents of the mixture, m. p. 160 – 180°

(above), was obtained in a state of purity. It separated from a considerable bulk of benzene in long, canary-yellow needles, m. p. 162–163° (Found: C = 72.7; H = 4.3. $C_{26}H_{20}O_6$ requires C = 72.9; H = 4.6 per cent.).

The less fusible isomeride appeared to be present in small amount only.

We wish to thank the Royal Society for a grant with which much of the cost of this investigation has been defrayed.

IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
SOUTH KENSINGTON. [Received, April 16th, 1923.]

CLXXI.—*A Note on the Photosynthesis of Amines.*

By OSCAR WALTER SNOW and JOHN FREDERICK SMERDON STONE.

IN a recent paper (this vol., p. 185), Baly, Heilbron, and Stern claim to have photosynthesised methylamine, pyridine, and piperidine by exposing a mixture of formaldehyde and ammonia (both 1.3*N*) to the ultra-violet light of a quartz mercury lamp. They also state that a coniine-like alkaloid was formed when 2*N*-solutions of the same substances were used.

Now the method they employed (see original paper, p. 190)* for the isolation of the photosynthesised bases involved the heating of the exposed solutions of ammonia and formaldehyde with excess of hydrochloric acid. The possibility that their results may be due to the normal interaction of ammonium chloride and formaldehyde seems to have been overlooked. This interaction has been studied by several investigators (Pfechl, *Ber.*, 1888, **21**, 2117; Brochet and Cambier, *Bull. Soc. chim.*, 1895, [iii], **13**, 392; Knudsen, *Ber.*, 1914, **47**, 2694), but more particularly by Werner (T., 1917, **111**, 844), who found that by heating concentrated solutions of ammonium chloride and formaldehyde he obtained much methylamine hydrochloride and smaller quantities of dimethylamine and tetramethylmethylenediamine hydrochlorides, the last giving rise to trimethylamine hydrochloride if the temperature was high enough. Methylmethyleimine hydrochloride was detected as an intermediate product.

In view of these facts, it seemed probable to us that, although the concentrations employed by Baly, Heilbron, and Stern are much less than those which Werner used, the same products might be expected to result in both cases.

* Wherever "the original paper" is referred to, that of Baly, Heilbron, and Stern, *loc. cit.*, is always meant.

Now Werner (*loc. cit.*) found that when a .12*N*-solution of ammonium chloride is gradually heated with commercial form. aldehyde to 104° the following reactions take place :—

- (1) $\text{CH}_2\text{O} + \text{H}_3\text{N}\cdot\text{HCl} = (\text{CH}_2\cdot\text{NH})\text{HCl} + \text{H}_2\text{O}.$
- (2) $(\text{CH}_2\cdot\text{NH})\text{HCl} + \text{H}_2\text{O} + \text{CH}_2\text{O} = \text{CH}_3\cdot\text{NH}_2\cdot\text{HCl} + \text{HCO}_2\text{H}.$
- (3) $\text{CH}_3\cdot\text{NH}_2\cdot\text{HCl} + \text{CH}_2\text{O} = (\text{CH}_3\cdot\text{N}\cdot\text{CH}_2)\text{HCl} + \text{H}_2\text{O}.$
- (4) $(\text{CH}_3\cdot\text{N}\cdot\text{CH}_2)\text{HCl} + \text{H}_2\text{O} + \text{CH}_2\text{O} = (\text{CH}_3)_2\text{NH}\cdot\text{HCl} + \text{HCO}_2\text{H}.$
- (5) $2(\text{CH}_3)_2\text{NH}\cdot\text{HCl} + \text{CH}_2\text{O} = \{(\text{CH}_3)_2\text{N}\}_2\text{CH}_2\cdot 2\text{HCl} + \text{H}_2\text{O}.$

The tetramethylmethylenediamine hydrochloride remains unchanged unless the temperature is raised to 160°, when the following reaction takes place,

$\{(\text{CH}_3)_2\text{N}\}_2\text{CH}_2\cdot 2\text{HCl} = (\text{CH}_3)_3\text{N}\cdot\text{HCl} + (\text{CH}_3\cdot\text{N}\cdot\text{CH}_2)\text{HCl},$
trimethylamine hydrochloride being formed. The methylmethylenimine hydrochloride is then converted into dimethylamine hydrochloride and formic acid (4).

In order to determine their behaviour to the physiological and colour tests used in the original paper, we have prepared specimens of the free bases, tetramethylmethylenediamine and methylmethylenimine, by the method of Henry (*Bull. Acad. roy. Belg.*, 1893, [iii], 26, 200) (Found: for tetramethylmethylenediamine, C = 58.63; H = 13.88. Calc., C = 58.82; H = 13.73 per cent.). The *picrate*, which has not previously been made, melted at about 95°, and was found to be very unstable, easily changing into dimethylamine *picrate* and formaldehyde (Found: for methylmethylenimine, C = 55.58; H = 11.64. Calc., C = 55.81; H = 11.63 per cent.). The *picrate*, already known, melted at 124° (127°, Duden and Scharff, *Ber.*, 1895, 28, 936).

Most of the chemical tests in the paper which Baly and his collaborators rely on, as establishing the probable presence of conine, are those recommended by Dilling (*Pharm. J.*, 1909, 29, 34). These are the Melzer, Marink (potassium cadmium iodide), Wagner (iodine in potassium iodide), and Nessler tests. We prepared the reagents required for these tests by the standard methods and applied them to the various amines with the results given in the table.

The results shown in this table indicate, in a very striking manner, how impossible it is to distinguish between these amines and conine by means of such reagents. It may be noted that in the Melzer tests the colour is taken up completely by ether (or toluene) in the case of conine only. The Wagner test, although more sensitive in the case of conine, is certainly not distinctive.

TABLE I.

	Molzer.		Marin.	Wagner.	Nessler.
	Uranium nitrate.	Copper sulphate.		Precipitate.	Precipitate.
Hydrochloride of Methylamino	—	—	—	Red-brown	Yellow
Dimethylamino	Orange-red; ether extract yellow	Brown; ether ex- tract brown	—	Red-brown	Yellow
Trimethylamino	Orange; ether ex- tract yellow	Brown; ether ex- tract brown	—	Brown-purple	Yellow; basic smell on warming
Tetraethylmethylen- diamino	Orange-red; toluene extract yellow	Brown; ether ex- tract brown	—	Brown-purple	Orange-red
Methylmethylenediamine	Yellow; toluene ex- tract yellow	Dirty green; ether extract indistinct	White, crystalline ppt.	Brown-purple	Yellow
Pyridino	—	—	—	Red-brown	Yellowish-white
Hyperidino	Orange; ether ex- tract yellow	Brown; ether ex- tract brown	—	Light brown	Pale yellow
Cofano	Orange-red; ether extract orange	Brown; ether ex- tract brown	White, crystalline ppt.	Brown-purple	Yellow; basic smell on warming

Description of Plate.

The plate shows a record of the contraction of two frog muscles stimulated simultaneously at fifteen second intervals. The lower muscle, poisoned by a 0.5 per cent. solution of tetramethylmethylenediamine hydrochloride, ceases at *A* to respond to stimuli arriving via the nerve. This is not a fatigue effect, since after five minutes' rest it still fails to respond to indirect (nerve) stimuli even with the secondary coil at 5 cm.

At *C*, both muscles are stimulated directly; both respond with the secondary at 5 cm., proving that the poisoning effect is primarily on the nerve ending. Again, the group of indirect stimuli at *D* fails to elicit any response from the lower muscle, even when the secondary coil is brought up to 2 cm. distance, whilst direct stimulation at *E* elicits responses at distances of 5 and 6 cm.

We now proceeded to repeat the work on the interaction of 2*N*-solutions of ammonia and formaldehyde exactly under the conditions employed by Baly and his collaborators (see original paper, p. 191), but without exposure to light, and obtained an "alkaloidal fraction" which gave positive results with all the above tests.

The only remaining piece of evidence in the original paper for the production of coniine is the physiological action of the product on the motor nerve-endings of a frog (*loc. cit.*, p. 193), namely, the "curare effect." We are much indebted to Mr. M. H. MacKeith of the University Pharmacology Department for advice on this part of the work and for kindly performing the necessary experiments and we should like to take this opportunity of tendering to him our most grateful thanks. His report is as follows:

"In the original paper (p. 193), Baly, Heilbron, and Stern adduce a pharmacological test in support of their recognition, by chemical means, of a coniine-like alkaloid in the products of a photocatalytic reaction described by them.

"The statement is made in their paper that the 'curare effect' (paralysis of the nerve-endings in striped muscle) is 'given only (their italics) by the curare alkaloids and by the members of the coniine group.' The former class of substances being excluded by appropriate chemical tests, the presence of an alkaloid of the coniine group is concluded.

"It was shown by Crum Brown and Fraser (*Proc. Roy. Soc. Edin.*, 1869, 6, 556) that certain of the organic derivatives of ammonium possess this 'curare effect.' It has since been demonstrated by many workers (Hofmeister, *Arch. exp. Path. Pharm.*, 1883, 16, 393; Marshall, *Trans. Roy. Soc. Edin.*, 1913, 50, 17; Zottermann, *J. Physiol.*, 1923, 57, xxi) that this effect is produced by a large number of compounds; by most quaternary ammonium salts, and by many other derivatives of quinquivalent nitrogen,

as well as by certain phosphorus and arsenic compounds with a similar stereochemical configuration. (Sollmann, 'Manual of Pharmacology,' 1922).

"It would appear, therefore, that the recognition of a coniine-like alkaloid is only valid on the exclusion of other substances capable of producing the same effect. Consequently, it is of interest to report that two of the already known products of the interaction of formaldehyde and ammonium chloride, namely, tetramethylmethylenediamine and methylmethyleimine, have been found to possess the 'curare effect.'

"The accompanying tracing shows, in the case of the hydrochloride of the tetramethyl compound, the manner in which the muscle loses its excitability to stimuli arriving by the nerve; also how, after it has ceased to respond to indirect (nerve) stimuli even with the secondary coil only 2 cm. distant, it responds by contraction on direct (muscle) stimulation at coil distances of 5 and 6 cm. At the same time, there is some direct action on the muscle substance, which is manifested by the diminution of height of the muscle response even on direct stimulation."

The pyridine, claimed to have been photosynthesised (see original paper, p. 190), was identified by means of a chloroplatinate which melted 15° too low, and by the smell produced on rubbing the hydrochloride with borax in a warm mortar. Since the method of separation of the supposed pyridine, by means of chloroform, is essentially that employed by Werner for the extraction of dimethylamine, tetramethylmethylenediamine, and methylmethyleimine, these substances were most probably present and it would be very difficult to detect pyridine in the presence of mixtures of such pronounced odour.

The production of methylamine in the experiments of Baly and his collaborators can be simply explained by the fact that it is the normal product of the Werner ammonium chloride-formaldehyde reaction.

We have obtained methylamine hydrochloride by evaporating 1:3N-solutions of ammonia and formaldehyde with hydrochloric acid, without exposure to light, and identified it by the melting points of mixtures of its hydrochloride and of its benzoyl derivative with authentic specimens of the respective compounds.

The formation of methylamine, by exposing a solution of ammonia saturated with carbon dioxide to ultra-violet light (original paper, p. 186), can be explained on the assumption that formaldehyde is first produced from the carbon dioxide by photosynthesis, as had previously been shown by Moore and Webster (*Proc. Roy. Soc.*, 1914, [B], **87**, 163, 556; 1918, [B], **90**, 168) and Baly, Heilbron,

and Barker (T.; 1921, **119**, 1025), the methylamine being then produced by the ordinary Werner reaction.

It should be stated that, in all the above experiments, the ammonia we employed was carefully freed from pyridine and phenol.

The results of the experiments described above seem to us to indicate that, although we have neither confirmed nor disproved the formation of a coniine-like alkaloid, of pyridine, or of piperidine from ammonia and formaldehyde under the conditions described by Baly, Heilbron, and Stern, the evidence advanced by them in support of their photosynthesis of these substances appears to us to be insufficient.

In conclusion, we should like to express our thanks to Dr. N. V. Sidgwick for very kindly reading through the proofs of this paper.

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OXFORD.

[Received, May 17th, 1923.]

(LXXII).—*The Action of Sodium Hyposulphite on Cupric Chloride in Aqueous Solution.*

By JAMES BRIERLEY FIRTH and JOHN HICSON.

DESCRIBING the action of sodium hyposulphite on copper sulphate solution, Schutzenberger (*Compt. rend.*, 1869, **69**, 196) states that in the cold the reaction gives rise to a red precipitate which may be either copper hydride or a mixture of this and metallic copper. The hydride reacts with the sulphurous acid produced and reduces it to hydrogen sulphide, being itself converted into sulphide. Myers and Firth (*Z. anorg. Chem.*, 1913, **80**, 98), repeating and extending Schutzenberger's experiments, were unable to detect the formation of hydride at any stage of the reaction. The product was either metallic copper, which may be highly pyrophoric, associated with a small amount of cuprous sulphide, or mainly the latter, according to the conditions of the experiment. The object of the present investigation was to study the reaction between an aqueous solution of cupric chloride and an aqueous solution of sodium hyposulphite. A series of preliminary experiments had indicated that the nature of the product was greatly influenced by the concentrations of the solutions used, and the temperature at which the reaction took place.

EXPERIMENTAL.

The reaction was carried out in an apparatus in which the operations of precipitation, filtration, and drying were performed in an atmosphere of carbon dioxide. The experiments here described

may be divided into two classes, namely, the influence on the course of the reaction of (a) the relative concentrations of the reacting solutions, (b) the temperature at which the reaction took place.

A solution of cupric chloride was prepared containing 7.5 grams of the pure crystallised salt in 100 c.c. A copper solution of this strength was used throughout the experiments. To 100 c.c. of the solution, 100 c.c. of a freshly prepared solution of pure sodium hyposulphite of a concentration varying from 1.5 to 30 grams per 100 c.c. was rapidly added. The reaction was allowed to proceed until no further apparent change either in the nature or bulk of the precipitate took place. The reaction was generally complete in ten to thirty minutes according to the temperature of reaction. In a number of experiments carried out for longer periods (up to twenty-four hours), the composition of the precipitate was substantially the same when the copper was in excess; in experiments in which the hyposulphite was in excess there was a slight increase in the sulphur content of the precipitate, but otherwise its general nature was the same.

The temperature of the reaction was varied from 15° to 75°. In the preparation of the hyposulphite solution at temperatures higher than 15°, the requisite amount of water was heated to about 3° above the required temperature and the necessary quantity of hyposulphite was added immediately before mixing the two solutions, thereby reducing as far as possible the decomposition of the hyposulphite prior to its coming in contact with the copper solution. At 15° and at 20°, on mixing the solutions, a white precipitate was first formed in all cases, but only at the lower concentrations of the hyposulphite solution was this precipitate permanent. As the concentration of the hyposulphite was increased, the white precipitate gradually changed through light brown, reddish-brown, dark brown to black, the actual stage at which the reaction stopped being determined by the concentration of the hyposulphite. At 50° and at 60°, the white precipitate appeared only at the moment when the solutions were brought into contact: almost immediately its colour became brown, then darkened, and finally was black. At 75°, on mixing the solutions, there was no immediate precipitate, the solution darkened in colour, and a dark brown or black precipitate was then deposited.

When the reaction was complete, the precipitate was rapidly collected, thoroughly washed with dilute sulphurous acid,* alcohol,

* In some of the earlier experiments in which cuprous chloride was the main product, it was found that if the precipitate was washed with water saturated with carbon dioxide or even with water alone, it darkened appreciably and the product contained oxide (compare Greger, *Z. anorg. Chem.*, 1901, 28, 154).

TABLE I.

Throughout the series, the copper solution contained 7.5 grams of crystallised cupric chloride in 100 c.c.

Temp.

Grams of sodium hyposulphite in 100 c.c. of solution.

Temp.	15°	30	50	60	75
Experiment	(1)	(2)	(3)	(4)	(5)
Copper	63.85	63.3	62.8	70.6	75.6
Sulphur	trace	0.1	1.6	2.6	3.3
Chlorine	36.00	35.6	35.6	27.0	25.0
Experiment	(12)	(13)	(14)	(15)	(16)
Copper	63.5	64.1	65.1	69.4	70.7
Sulphur	1.1	1.92	7.8	7.6	6.2
Chlorine	35.2	34.7	25.25	23.1	22.7
Experiment	(22)	(23)	(24)	(25)	(26)
Copper	78.5	77.9	76.6	73.1	69.6
Sulphur	21.5	18.4	18.7	20.4	22.2
Chlorine	trace	4.3	3.4	4.3	7.7
Experiment	(29)	(30)	(31)	(32)	(33)
Copper	80.44	79.3	74.1	72.0	68.3
Sulphur	18.4	18.7	19.6	22.7	18.2
Chlorine	trace	1.5	6.3	6.0	6.6
Experiment	(36)	(37)	(38)	(39)	(40)
Copper	75.6	76.7	76.1	75.3	74.6
Sulphur	22.1	16.3	17.9	17.2	19.2
Chlorine	trace	6.3	6.6	4.1	7.1
					4.6
					7.0
					3.5
					6.8
					90.2
					77.8
					23.4
					1.1
					trace
					31.7
					67.2
					(21)
					22.5
					15.0
					(9)
					87.7
					73.2
					(10)
					26.5
					30.5
					68.9
					(11)
					30.0

alcohol and carbon disulphide, and ether, respectively, and dried over calcium chloride in an evacuated desiccator. The filtrate invariably contained sulphate and free acid.

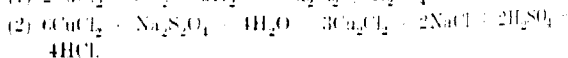
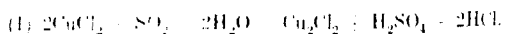
When quite dry, the precipitates were analysed. The results obtained are set out in the following table, in which the effect of temperature on the composition of the precipitate for a definite hyposulphite concentration is given in the vertical columns and the effect of concentration of hyposulphite at constant temperature is given in the horizontal divisions.

The results show that at 15°, for concentrations 1.5–4.5 grams of hyposulphite per 100 c.c., the precipitate is essentially cuprous chloride; with further increase in the concentration of the hyposulphite, the amount of chloride rapidly diminishes and free copper appears in the precipitate. When the concentration of the hyposulphite has reached 10.5 grams per 100 c.c. (experiment 7), the precipitate contains no chloride and is essentially metallic copper associated with a small amount of sulphide. As the concentration of the hyposulphite is further increased, the amount of sulphur is increased, until finally, when the concentration has reached 30 grams per 100 c.c., the precipitate has the composition of cupric sulphide (experiment 11). At 30°, the results are similar except that the sulphur contents are slightly higher and chloride persists throughout the series.

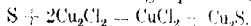
At 50°–75°, the precipitates at the lower hyposulphite concentrations are essentially cuprous sulphide, which passes into cupric sulphide with increase in hyposulphite concentration. The precipitate is in all cases associated with various amounts of chloride. Although in the experiments at 75° there was no appreciable amount of free copper in the precipitate, yet in many cases a thin film of metallic copper was deposited on the sides of the reaction vessel.

Discussion of Results.

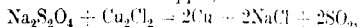
Owing to the fact that sodium hyposulphite in solution readily decomposes, giving rise principally to thiosulphate, sulphurous acid, and free sulphur, the reaction with a solution of cupric chloride is necessarily complex. Up to 30°, for low concentrations of hyposulphite (cupric chloride in excess), the reaction is a comparatively simple reduction of the cupric chloride and may be represented by the equations



The solution thereby contains free sulphuric and hydrochloric acids. Wardlaw and Pinkard (T., 1922, **121**, 210) have shown that cuprous chloride reacts with sulphur in presence of dilute hydrochloric acid at approximately 95°, with the production of cuprous sulphide, the reaction being represented by the equation



This reaction would explain to some extent the production of cuprous sulphide with rise of temperature and also the persistence of chloride in the precipitate. It is improbable, however, that the whole of the sulphide is derived from this source; cuprous salts such as the hyposulphite and thiosulphate (compare Myers and Firth, *loc. cit.*) will be produced and, being unstable, will readily decompose with the production of sulphide. Up to 30°, in presence of a slight excess of hyposulphite, the cuprous chloride first formed is further reduced to metallic copper,



whilst in presence of further excess of hyposulphite the finely divided copper is converted into cupric sulphide,



Owing to the continuous change in the conditions as the reaction proceeds, it is impossible to represent the complete phenomena by any simple set of equations. The reactions set out above represent only the main types; others of more complex but of less fundamental character are taking place simultaneously, tending in the main to yield the same final products.

Summary.

1. At temperatures up to 30°, a solution of cupric chloride is reduced by sodium hyposulphite to cuprous chloride, which is permanent in presence of excess of cupric chloride.

2. With increasing amounts of hyposulphite the cuprous chloride is first reduced to metallic copper and finally converted into cupric sulphide.

3. At temperatures from 50–75°, the final product, if cupric chloride is present in excess, is mainly cuprous sulphide, which is converted into cupric sulphide by excess of sodium hyposulphite.

UNIVERSITY COLLEGE, NOTTINGHAM.

[Received, April 27th, 1923.]

*Baeyer Memorial Lecture.*¹

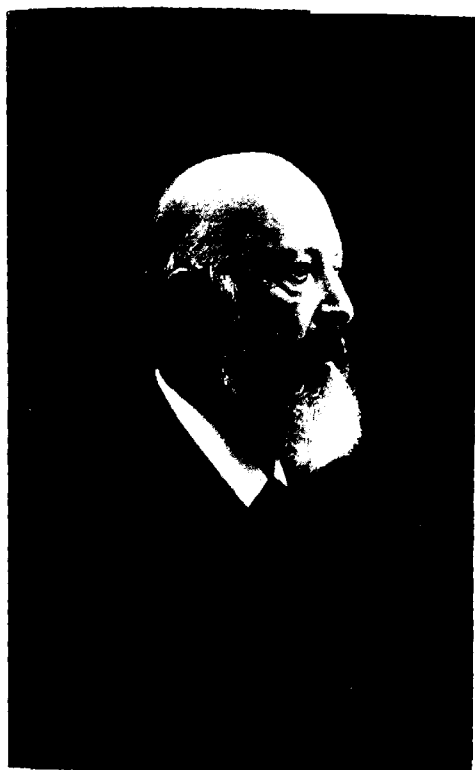
DELIVERED ON MAY 10TH, 1923.

By WILLIAM HENRY PERKIN, LL.D., F.R.S.

THE survey of the present position of Chemistry, and more particularly of Organic Chemistry, cannot fail to leave the impression that a definite period in the development of the Science has closed with the decease of Adolph von Baeyer and of Emil Fischer. The influence of these men has been profound, mainly, no doubt, because of the immense amount of work of fundamental importance which they have left behind, but to a scarcely less degree by reason of their influence as teachers.

Their methods as investigators and teachers were remarkably similar in almost every particular, as indeed might be expected when it is remembered that Emil Fischer was not only a pupil, and perhaps the most distinguished pupil, of Baeyer, but was also, for a long period, Baeyer's principal assistant, and he thus had every opportunity of learning the methods of teaching and the art of experimenting characteristic of his great teacher. In charge of large laboratories overrenowned with students, especially in later years, the first care of both these men was to see that the foundations of the Science, whether the section was Inorganic or Organic, were systematically and very thoroughly taught. With this object in view, the professor himself undertook the first elementary course of lectures and placed his most distinguished Privatdozent in charge of the teaching of practical Inorganic Chemistry, and thus the foundations were truly laid and, when the study of Organic Chemistry was subsequently undertaken, it was not until a sound knowledge of Inorganic Chemistry had been secured. Great stress was laid, both by Baeyer and by Emil Fischer, on a very thorough training in manipulation and the technique of experimenting, with the result that when the time came to engage in original work, the student was in a position to undertake his task with every prospect of success and needed only the minimum of supervision. The life and work of Emil Fischer has been ably dealt with by Dr. M. O. Forster in a Memorial Lecture delivered before the Society of

* In compiling this Memorial Lecture, I have obtained much information from the "Erinnerungen aus meinem Leben," which Baeyer himself wrote as an Introduction to the two volumes of collected papers published in 1905 on the occasion of his seventieth birthday, by his pupils and friends. I have also made free use of Adressen delivered by Professor Willstätter in 1915 and 1917 and published in *Die Naturwissenschaften* and the *Zeitschrift für angewandte Chemie*, copies of which the author kindly placed at my disposal.



Welf Berger

October 28th, 1920; and it is now my pleasant duty to give, even if very inadequately, a brief sketch of the life and work of my revered teacher, Adolph Baeyer. While we are passing in review the wonderful achievements of Baeyer, and attempting to follow the sequence of his brilliant researches, it may be useful to remember the conditions which prevailed during the time that his career as a teacher and investigator was developing.

Baeyer's long life covered the period from the first railway train almost to the present day, from the time of Faraday's laws of electrolysis to the discovery of the inert gases and of the radioactive elements. He was born in 1835, shortly after the publication of the synthesis of urea by Wöhler, the discovery of aniline and phenol in coal tar by Runge, and the preparation of benzene from benzoic acid and its nitration by Mitscherlich. While he was still a boy, Liebig and Wöhler published their famous paper on benzoyl which led to the enunciation of the radical theory, and the completion of his thesis for the Degree of Doctor, "Ueber die Verbindungen des Arsens mit dem Methyle," coincided almost exactly with the publication of Kekulé's great work "Ueber die Konstitution und die Metamorphosen der chemischen Verbindungen und über die chemische Natur des Kohlenstoffs."

During the period when Baeyer was Privatdozent in Berlin, the benzol theory of Kekulé and the discovery of the periodic arrangement of the elements by Lothar Meyer and Mendeléev appeared, and at the time when Baeyer was at Strassburg, van't Hoff published his "Chemistry in Space."

A great reader of the literature, Baeyer absorbed everything directly it was published and immediately discussed any development, which seemed to him to be important, with those engaged in research in his laboratories, and it is stated that, in his later years, the isolation of the inert gases and the discovery of radium and radioactivity were subjects which particularly delighted him. But it was the atmosphere of the laboratory which was Baeyer's joy, and those who have been privileged to see the great man going about from day to day among his test-tubes and preparations are not likely to forget the experience.

Baeyer's first papers—"Notiz über idiochemische Induction" and "Ueber das Methylechlorür"—appeared in 1857 (*Annalen*, 1857, 178 and 181), while he was working in Heidelberg in von Liebig's laboratory, and his last paper, published when he was fifty years of age, is to be found in the *Annalen* of 1915 (407, 1915). During this period of fifty-eight years he published a steady stream of researches, each one characterised by some observation of interest; and many of these communications have, of course,

become classical and have left an indelible impression on the progress of our Science.

Johann Friedrich Wilhelm Adolph Baeyer was born on October 31st, 1835, in Berlin. His father, Johann Jakob Baeyer, was a captain in the Prussian army, and his mother, Eugenie, was a daughter of Julius Eduard Hitzig, Director of the Criminal Court in Berlin. In his young days, Baeyer came much into contact with men well known in the literary circles of the time and also with prominent historians who visited regularly at his father's house, but in his "Erinnerungen aus meinem Leben," he states that he found little which really interested him in studies of this kind. It is remarkable that even as a boy he developed a strong desire to study nature, and this instinct was greatly assisted by the frequent journeys which he took into the country with his father during the school holidays. On these occasions, his father was usually occupied in making trigonometrical observations, which were to form part of a general survey of the land, and the boy was left much to himself with nature as his playground. Doubtless it was in this way that the fondness for botany was acquired which remained throughout his life.

The first chemical experiments seem to have been made at a very early age and to have caused not a little inconvenience to his family and the visitors to the house. On one occasion the state of the atmosphere in the house was such that the poet Paul Heyse, who was a visitor at the time, had occasion to remark :

"Es stinkt in diesem Haus gar sehr
Das kommt vom Adolph Baeyer her."

His actual introduction to Chemistry seems to date from his ninth birthday, when his father, having found it impossible to keep him from carrying out wild experiments, to the continual annoyance and danger of the rest of the family, thought it wise that he should go through some definite course and therefore gave him a copy of Stockhardt's "School of Chemistry," which was a very popular book at that time.

Baeyer relates that he was allowed to fit up a small room in the house as a primitive laboratory and that, with the aid of a school friend, whose main business seems to have been to clean the scanty stock of apparatus, he had soon worked through the whole of Stockhardt. It was in 1847, when he was twelve years of age, that he made his first new substance, a crystalline double salt of copper and sodium carbonates, and this he obtained accidentally, in fine, deep blue crystals, by mixing copper sulphate with sodium carbonate and allowing the solution to stand for some days. This salt was

investigated in 1851 by Struve and by Gentile, who made it in the same way as Baeyer had done, and they showed that it has the composition $\text{CuCO}_3 \cdot \text{Na}_2\text{CO}_3 \cdot 3\text{H}_2\text{O}$.

The more serious study of Science seems to have begun when Baeyer was about thirteen years of age, and was due to his coming under the influence of K. Schellbach, one of the teachers at the school he was attending, who subsequently became well known on account of the influence he exercised on the improvement of the teaching of science in general and in the Prussian schools in particular. Under Schellbach, of whom he speaks in glowing terms and whose assistant he subsequently became, Baeyer studied Mathematics and Physics with the greatest keenness and became so interested in these sciences that he seriously considered devoting his main attention to them when the time came to go to the University. He seems, however, still to have kept his interest in Chemistry, for he relates that he also worked through all the experiments described in Wöhler's "*Leitfaden der organischen Chemie*."

A year or two later, when he was fifteen, Baeyer seems, for some reason which is not quite apparent, to have lost much of his interest in Physics and Chemistry and to have devoted all his spare time to the study of Botany and Geology, and so keen did he become that when seventeen he undertook, in company with Ferdinand von Richthofen, who was two years his senior, a six months' tramp from Trieste through Dalmatia and Montenegro and back over the Eastern Alps, with the main object of collecting material to help him in his further studies. However, this change of occupation, which no doubt was very useful training, did not last long, for, after the usual period of military service, we find Baeyer coming to the definite conclusion that Chemistry was to be the work of his life.

With a view to the systematic study of Chemistry, he made up his mind that the best thing to do, in the first place, was to proceed to Heidelberg and study under Bunsen, whose laboratory was then the most famous in Germany, and there he came at once into contact with Roscoe, Lothar Meyer, Lieben, and Beilstein, who were working in Bunsen's laboratory at the time. Partly in consequence of the early experience gained in the small laboratory in his father's house and partly as the result of hard work in Heidelberg, he was informed at the end of the first Semester, by the assistant under whom he worked, that he had made sufficient progress in qualitative and quantitative analysis to start a piece of original work, and the first task given him was to help Bunsen and Roscoe with their well-known experiments on the combination of chlorine and hydrogen under the influence of light, and the results of these investigations were published in 1857 (*Annalen*, 103, 178). In the same volume

of the *Annalen* (p. 181), Baeyer published, moreover, a short account of a research on methyl chloride, also undertaken at the suggestion of Bunsen.

Bunsen was desirous of finding out whether methyl chloride prepared by the chlorination of methane was the same substance as is obtained when hydrochloric acid acts on methyl alcohol, and, if so, whether it is identical with the chloromethyl which results from the action of heat on the hydrochloride of cacodylic acid. During the course of this investigation, Baeyer discovered the crystalline hydrate of methyl chloride, $\text{CH}_3\text{Cl} \cdot 7\text{H}_2\text{O}$, but although he was able with its aid to show that the methyl chloride from cacodylic acid is the same as that from methyl alcohol and hydrochloric acid, he was unable to prove identity with the product of the chlorination of methane, mainly on account of the complexity of the product he obtained as the result of that chlorination. The proof of identity was, however, supplied two years later by Berthelot (*Annalen*, 105, 242). When he had completed these researches, Baeyer began to feel that he had reaped as much benefit as he could hope to do from Bunsen's laboratory: he had learnt inorganic analysis as well as the methods of gas analysis, which were being developed by Bunsen at that time, but he had not obtained much insight into theoretical chemistry, and especially had made little progress with the study of Organic Chemistry, mainly because Bunsen had lost much of his earlier interest in Organic Chemistry and no longer encouraged its study.

At that time, August Kekulé, who was then Privatdozent in Heidelberg, had rented a small house and converted one room and the kitchen into a primitive laboratory, and Baeyer asked permission of Kekulé to be allowed to work with him in this laboratory as his first pupil. Thus it came about that Baeyer, although he worked for rather less than two years in this private laboratory, came to be known as a pupil of Kekulé. With the scanty accommodation and small stock of apparatus available, Baeyer continued his researches on cacodyl trichloride, and during the course of these experiments he accidentally discovered arsenic methyl chloride. Not grasping the dangerous nature of the substance he had made, he investigated its odour, with the result that he fainted and nearly lost his life.

Having completed this research, Baeyer returned to Berlin in 1858 and presented it, as was the custom at the time, in Latin, and under the title "*De arsenici cum methylo conjunctionibus*," as his thesis for the Degree of Doctor. The difficulty of the work was apparently not realised, because the thesis was coldly received, and this want of appreciation, aided by a poor oral examination, resulted

in a second class (*magna cum laude*) which Baeyer says was as much as he had expected.

Kekulé had in the meantime been called to Ghent as the successor to Stas, and Baeyer relates that in the winter 1858/59 he decided to follow Kekulé in order to work in his new laboratories, particularly with a view to the further study of Organic Chemistry, about which, he says, he still knew very little.

On the way from Heidelberg to Ghent he made the acquaintance of a manufacturer named Adolph Schlieper, who had worked on uric acid under Liebig, and, on parting, Schlieper gave him a box containing his preparations with the request that he would continue their investigation. The practical work which Baeyer could do in Kekulé's laboratory in Ghent was, however, much interfered with by military service, but he nevertheless managed to finish a research on the esters of allophanic acid, which he had begun in Heidelberg, and to find time to make a careful examination of the contents of the box which Schlieper had given him.

One result of the experiments which he did with these specimens was the discovery, in 1860, of *pseudo*-uric acid, a valuable piece of work which he published in conjunction with Schlieper. He made many attempts at the time to convert this acid into uric acid by the elimination of water, but in vain, and it was not until 1895 that this important step in the synthesis of uric acid was accomplished by Emil Fischer by heating with anhydrous oxalic acid.

Two years later, Fischer showed that this change may be more conveniently brought about by heating with much dilute (20 per cent.) hydrochloric acid, a reagent which Baeyer had also employed, but unsuccessfully, the reason of the failure being, as he himself states, that the acid he had used was too concentrated.

The Berlin Period.

In the spring of 1860, Baeyer returned to Berlin, became Privatdozent, and shortly afterwards received the appointment of Teacher of Organic Chemistry in the Gewerbe-Institut in the Klosterstrasse, a modest and badly paid post which he held for twelve years. In this Institute, he organised a laboratory for practical work and gradually collected together a number of keen and zealous workers, among whom were Graebe, Liebermann, and Victor Meyer. There can be no doubt that it was in this unpretending laboratory in the Klosterstrasse that Baeyer gradually acquired that keen penetration and marvellous skill in experimenting which subsequently made him so famous.

During these years Baeyer continued his researches on uric acid and its derivatives, and gradually brought order out of the chaos

which had reigned for so long in this difficult and puzzling group; subsequently Emil Fischer completed the work by synthesising all the more important members of the purine series and it may be claimed that, thanks to these brilliant investigators, this important chapter is now as clearly understood as any section of Organic Chemistry.

It is probably true that much of the work on which Baeyer concentrated his attention during his subsequent career at Strassburg and Munich owes its origin in one way or another to the preliminary experiments which were carried out in the laboratory in the Klosterstrasse.

Thus, among the researches published in 1870 from that laboratory, we find the reduction of indigo to indole, by distillation with zinc dust, and the synthesis of indigo from isatin. The discovery of this method of reduction by distillation with zinc dust had far-reaching results, for in the same year and in the same laboratory, Graebe and Liebermann succeeded, by its aid, in reducing the colouring matter of the madder plant to anthracene—an achievement of immense importance which was always a source of great satisfaction and delight to Baeyer. This result enabled Graebe and Liebermann to bring about the synthesis of alizarin from coal-tar anthracene, a remarkably fine piece of work, which laid the foundation of the alizarin dyestuff industry, not only in Germany, but also in this country.

The long and difficult researches on uric acid and its derivatives, which had occupied so much of his attention for so many years, coupled with his previous training in botany, had the interesting result of causing Baeyer to turn his attention to the problems of physiological chemistry and especially to the question of the assimilation of carbonic acid by plants and the mechanism of the synthesis of the sugars.

The paper "*Ueber die Wassereutziehung und ihre Bedeutung für das Pflanzenleben und die Gährung*," published in 1870 (*Ber.*, **3**, 63), is full of the most interesting and remarkable theoretical views. In this communication, the brilliant and entirely novel suggestion is made that the formation of sugar in the plant is due to the reduction of carbonic acid, in the green leaves and under the influence of light, to formaldehyde, which then undergoes condensation with the formation of grape sugar. This condensation of formaldehyde to a sugary substance by the action of alkalis had shortly before been actually achieved by Butlerow. Baeyer seems also to have inclined rather to the view that, as chlorophyll is so similar in many ways to hæmoglobin and the latter has great affinity for carbon monoxide, it is probable in the formation of formaldehyde

that chlorophyll first dissociates the carbonic acid of the atmosphere, liberating oxygen and combining with the carbon monoxide. Then the combined carbon monoxide is reduced by the constituents of the cell to formaldehyde. Very interesting and suggestive are the views which Baeyer expresses in this paper on the question of the nature of fermentation, during the development of which he put forward a formula for grape sugar which is identical with that employed at the present day. When the rudimentary state of the knowledge of structural Chemistry which obtained at that time is taken into account, the theoretical views contained in this paper can only be described as an extraordinary achievement. This same paper is also remarkable on account of the views advanced to explain the mechanism of the elimination of water in the course of simple decompositions such as, for example, the conversion of glycerol into acrolein, processes which were at that time difficult to understand; and it is clear that these views had an important influence on the development of that long series of researches on "condensation" which occupied so much of Baeyer's attention during subsequent years. The study of the phenomenon of condensation seems to have had its actual origin in an investigation of the action of acids on acetone (*Annalen*, 1866, **140**, 297), in the course of which Baeyer worked out the conditions for the formation of mesityl oxide and phorone, and it is most interesting to read the views which he expresses at the end of the paper on the mechanism of these condensations and the constitutions of these substances.

This research gradually developed in all kinds of directions until it came to include all sorts of condensations very far removed from the original acetone condensation: such, for example, as the condensation of hydrocarbons and phenols with aldehydes under the most varied conditions. It was in this way that the phthaleins were discovered, and in describing how phthalic anhydride came to be employed in these condensations, Baeyer explains that the first object of these experiments was an attempt to condense together phenolic substances in the hope of synthesising plant products, during the course of which he thought that phthalic anhydride might perhaps prove useful as a mild dehydrating agent. This led to the discovery of many valuable dyestuffs such as gallein, the condensation product of phthalic anhydride and pyrogalllic acid, and of cœrulein, the green anthraene dyestuff obtained by heating gallein with sulphuric acid. These and other well-known members of the group, of which it is only necessary to mention fluorescein, eosin, and the rhodamines, are among the most beautiful of all the artificial colouring matters, and for this reason they soon became and still are of immense technical importance.

The Strassburg Period.

The position which Baeyer held at the *Gewerbe-Institut* in the Klosterstrasse was in many ways a difficult one: the authorities apparently did not realise the fine work which was being done, and when it was suggested, after a stay of ten years, that some addition might well be made to the quite inadequate salary attaching to the post, the suggestion was rudely refused.

In spite of this, when offered the Chair of Chemistry at Königsberg in 1870 as successor to Werther, Baeyer elected to remain in Berlin, even although the conditions were not to his liking. The great change from the rather unimportant post in the Klosterstrasse to a Chair in a University was, however, soon to come, and in 1872 Baeyer received and accepted the call to Strassburg, as Professor of Chemistry and Director of new laboratories, which, although not then in existence, were to be erected immediately. It is interesting to note what a remarkably able staff there was in Strassburg at that time, for apart from Baeyer and Heinrich Rose, Physics was represented by Kundt, Röntgen, and Exner, and Groth was the mineralogist.

Perhaps the most important event in the early days in Strassburg was the arrival of Emil and Otto Fischer, who, attracted by the fame of Baeyer, decided in the autumn of 1872 to settle in Strassburg and study Chemistry in the old laboratories which were still in use. At that time the instruction in Inorganic Chemistry was in the able hands of Rose, who had recently come from Heidelberg, and he at once introduced the system of teaching, and especially the analytical methods, of Bunsen. Emil Fischer, in his "*Erinnerungen aus der Strassburger Studienzeit*," relates how attractive these simple and rapid methods of analysis were in comparison with the long and tedious processes he had been taught to use while he was studying at Bonn.

When the time came to begin original work, Baeyer suggested to Emil Fischer that he should continue the investigation of the two hexahydromellitic acids—hydromellitic acid and isohydromellitic acid—which Baeyer had obtained from mellitic acid from Hopfgstein in 1870 (*Monatsh.*, Suppl. 7, 1). With this object in view, Baeyer handed over to Emil Fischer the large supply of Hopfgstein which he had gradually collected, but the research, unfortunately, came to nothing. One reason for this was the want of experience of the methods of manipulation in Organic Chemistry which Emil Fischer then had at his command, but the main cause of the failure was an accident due to the floor of the old laboratory giving way, with the result that Emil Fischer fell through, while he was carrying the

product of the reduction of half a kilogram of mellitic acid and a large quantity of mercury. It thus became necessary to make a start with another piece of original work and this again was suggested by Baeyer.

At that time, the whole laboratory was engaged in the investigation of the condensation products of aldehydes with aromatic hydrocarbons and phenols, which Baeyer had begun in Berlin, and Fischer now joined hands with the others and with such success that he was shortly afterwards able to publish the results of his investigation in the *Berichte* (1874, 7, 1211) under the title "Ueber Fluoresceïn und das Phthalœïn des Orcëins." In 1873, the attendance in the chemical laboratory had increased to such an extent that it became absolutely necessary to provide additional space and, as the result of urgent representations made to the authorities, building was commenced immediately and progressed so rapidly that the new laboratories were in active use during the following year.

Partly because of the interruption of work due to the building of these new laboratories and partly on account of the large amount of time which had to be given to the organisation of the courses of study, the two and a half years at Strassburg must be looked upon as merely a transition stage in the career of Baeyer. It is true that many of the researches which had been begun in Berlin were developed in various directions and with very interesting results in the Strassburg laboratories, but very little actually new work was started. One discovery of far-reaching importance must, however, be recorded, and that is the first preparation of nitrosodimethylaniline and its conversion into nitrosophenol, which Baeyer and Caro published in 1874 (*Ber.*, 7, 809, 963).

During the early months of 1875, Baeyer was invited to the Chair of Chemistry in Munich, as the successor to Liebig, and although he ultimately accepted the invitation, he seems to have taken this step with a good deal of hesitation and only after very careful consideration. He states in his "Erinnerungen" that he would not have hesitated in ordinary circumstances for a moment, because of the much greater importance of Munich as a University and also because he considered it an honour to be asked to follow Liebig. But the political situation in Bavaria was not to his liking, and he also felt that it was not quite fair to Strassburg to leave the laboratories he had just built when he had been there for so short a time.

In these circumstances, he travelled to Berlin in order to consult the many friends he had made during his long stay in that city, and, as all were unanimous in advising him to accept the invitation to

Munich, he decided to make the move, and thus the Strassburg period came to an end.

The Munich Period.

The situation which confronted Baeyer on his arrival in Munich was in many ways an exceptionally difficult one. When Liebig, in 1852, accepted the invitation of König Max to become Professor of Chemistry in Munich, it was on the distinct understanding that he should be completely free from laboratory teaching. It is remarkable that, in spite of the magnificent experimental work which was the outstanding feature of his earlier years, Liebig's interest in experimental investigation should have disappeared so completely that he no longer thought it necessary that the Professor of Chemistry in Munich should have a laboratory of his own or indeed a laboratory of any kind for the training of students. His main interest, in his later years, seems to have been confined to lecturing and to studying the applications of Chemistry to Agriculture and Medicine. It is true that his lectures were very popular and were attended by the King and the Royal Family and also by the Ministers of State, and they seem also to have been largely patronised by the general public.

As there was no laboratory, there were necessarily no students of Chemistry, and it was evident that Liebig had no desire to continue the famous tradition of the Giessen School. Whilst it is difficult to understand Liebig's attitude towards laboratory teaching, it is still more amazing that the Government of the day should have consented to allow this state of things to continue for more than twenty years (1852-75).

On his arrival, Baeyer recognised at once that his first task was to provide for the proper teaching of practical Chemistry and, in order to do this, it was clearly necessary to proceed at once with the plans for suitable laboratories. It is evidence of the largeness of view which Baeyer took of the situation, that the laboratories he designed were laid out on a scale which must have appeared quite out of proportion to the needs of those days. However, his plans were adopted and the building, which was begun early in 1876 and was ready for occupation in the autumn of the following year, is still a fine building and admirably suited for its purpose. The laboratories were indeed so well designed in all their details that they long served as a model for the other laboratories which gradually sprang up in all the principal University towns in Germany.

In organising the courses of instruction in practical Chemistry, the Inorganic section of the subject was placed in the hands of Jakob Volhard, and his first successor in the line of famous chemists

who taught Inorganic Chemistry in Munich was Emil Fischer. The teaching of Organic Chemistry seems, from the beginning, to have been entirely in Baeyer's own hands and he also delivered the elementary lectures in Inorganic Chemistry and indeed continued to do so right up to the time of his resignation in the year 1915. The research work carried on during the first ten years in Munich was mainly devoted to the continuation of the various investigations in the group of the phthaleins, as well as to the development of the series of researches on the condensation of aldehydes with phenols, and particularly to the first really serious study of the indigo problem. It was during these years that the mechanism of the condensation of phthalic anhydride with phenols was clearly established. In the first place, it was shown that phthalide, which had been thought to be an aldehyde, was in reality a lactone, and subsequently phthalophenone, which Friedel and Crafts had obtained from phthalyl chloride by condensation with benzene in the presence of aluminium chloride, was also shown to be a lactone and was recognised as the parent substance from which the phthaleins were derived.

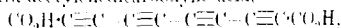
In a lecture delivered at the Hofmann House in Berlin on October 20th, 1900, Baeyer states that the original impulse to work on indigo can be traced to an incident which occurred when he was only thirteen years of age. It seems that on his thirteenth birthday he was given a two-thaler piece with which he bought a lump of indigo, and he appears to have been immediately fascinated with the properties of the substance, and this fascination remained until he had completely solved the chemistry of the colouring matter. He did not, however, begin to investigate indigo experimentally until 1865, and then he carried out and published the results of a series of experiments which were very remarkable, especially when the state of Organic Chemistry at that time is taken into account. In the course of these experiments, he examined the properties of indigo in detail and prepared several important derivatives, among which was isatin. He showed that isatin on reduction yields first diindole and then oxindole, and that these substances, on distillation with zinc dust, are reduced to the parent substance, indole.

In 1870, in conjunction with Emmerling, he achieved the first synthesis of indigo, which, as is well known, was the result of heating isatin chloride with phosphorus and hydriodic acid. In view of the extraordinary interest attaching to this discovery, it is remarkable, and indeed unlike Baeyer, that the matter was at the time not immediately followed up, but this was due to the fact that Baeyer put aside the work out of consideration for Kekulé, and thus it came about that nothing more was done with the indigo

problem for eight years. In 1869, Kekulé had published a paper in which he stated that he proposed to carry out a series of experiments having for their special object the synthesis of isatin, and, in order not to interfere with this work, Baeyer decided to leave the further development of the whole indigo problem to Kekulé. However, nothing came of Kekulé's work, and as no one else appeared to be occupied with the indigo problem, Baeyer, soon after his arrival in Munich, again took up the subject, and between 1878 and 1884 those classical researches on indigo and its derivatives appeared which will always be intimately associated with the name of Baeyer. These investigations must always rank among the most brilliant in the whole range of organic analysis and synthesis; for not only did they throw a flood of light on the constitution of indigo and clearly demonstrate its close relationship to indole, but they also gave to the world those marvellous syntheses which are the wonder of every chemist who repeats them. It has already been mentioned that the first synthesis of indigo (1870) was the conversion of isatin chloride into indigotin by reduction with hydriodic acid and phosphorus, but this process, interesting though it was, did not proceed smoothly enough to allow of its acceptance as definite proof of the constitution of the colouring matter. Of far greater importance were the syntheses (1880) from *o*-nitrophenylpropionic acid by the action of alkaline reducing agents and the synthesis from *o*-nitrobenzaldehyde and acetone which Baeyer and Drewsen subsequently published in 1882. But the most elegant synthesis, also published in 1882, is unquestionably that from di(*o*-nitrophenylacetylene), a brilliant piece of experimenting which even Baeyer has seldom surpassed. These synthetic processes very naturally attracted the attention of the German dye works, and a great amount of work was feverishly carried out by an army of research chemists in the hope that the development of these syntheses might lead to a successful process for the manufacture of indigo. But in the technical application of the results of his researches Baeyer took little if any active part, his interest in indigo seems to have completely disappeared so soon as he had finished his scientific investigations, and he was more than content to leave any technical development and pecuniary advantage to others. The fact that Baeyer would not assist in solving the very great difficulties which beset the manufacturer, in his desire to discover a commercially successful process for the manufacture of indigo, caused a good deal of ill-feeling, particularly in view of the fact that very large sums of money were being spent on experimental work, and process after process was tried only to be ultimately given up as too expensive. In his own account of his indigo researches, Baeyer states that

in 1885 he began to feel severely the mental strain inseparable from his long series of investigations in this group, and he became indeed so exhausted and acquired such a distaste for the whole subject that he determined to have no more to do with it and to seek relief in a complete change of work. The first subject which now occupied his attention was an investigation in the polyacetylene group which may have had its origin in a series of experiments on simple acetylene derivatives which Berend and Liebermann had carried out in his laboratories during the Berlin period. The object of the work seems to have been a desire to join molecules of acetylene together until a substance was produced which contained so small a proportion of hydrogen that it might be expected to exhibit close resemblance to the diamond: but Baeyer recognised that such a substance would, in all probability, prove to be a very explosive modification of the diamond. Baeyer used to say that he thought it conceivable that the diamond might contain a minute amount of hydrogen, since it had been stated that traces of water were always produced when diamond dust was burned in oxygen. From this idea of adding acetylene grouping to acetylene grouping there arose a most brilliant experimental investigation on the polyacetylenes and polyacetylenecarboxylic acids which, owing to the explosive nature of the substances dealt with, had to be carried out with minute quantities of material. There is probably no piece of work in which Baeyer's experimental skill is more strikingly exemplified than in the papers "Ueber Polyacetylenverbindungen," published in 1885.

Starting with dibromosuccinic acid, Baeyer converted this by the action of alkalis into acetylenedicarboxylic acid and then by elimination of carbon dioxide into propargylic acid. The copper derivative of the ester of this acid yielded, on oxidation with ferricyanide and subsequent hydrolysis, diacetylenedicarboxylic acid, $\text{CO}_2\text{H}\cdot\text{C}\equiv\text{C}\cdot\text{C}\equiv\text{C}\cdot\text{CO}_2\text{H}$, from which diacetylene, $\text{CH}\equiv\text{C}\cdot\text{C}\equiv\text{CH}$, was obtained and, on repeating the process with this acid, tetra-acetylenedicarboxylic acid,



resulted as a colourless, crystalline substance which became rapidly black on exposure to light and was, in anything but very small quantities, spontaneously explosive, so that it was quite out of the question to hope to lengthen the acetylene chain any further than this. It was the author's good fortune to be allowed to take part in and watch these experiments, and the experience of the experimental skill with which Baeyer carried out these very ticklish operations, with no other apparatus than test-tubes and glass rods, is to this day a very lively recollection.

At the end of the second paper on polyacetylene derivatives, a section is devoted to "Theoretische Betrachtungen," and this contains the famous "Spannungs Theorie," as well as the theory of the treble linking.

The Spannungs Theorie deals with the theoretical considerations underlying the stability of the various rings containing multiples of methylene such as ethylene, trimethylene, tetramethylene, pentamethylene, hexamethylene, etc., and is based, as is well known, on the strain to which the valencies of carbon, directed from the centre to the corners of the tetrahedron model, must be subjected in order to bring them into the configuration of these various closed rings. This theory has been of immense value and a great incentive to further work on closed rings, and although the original conception has been somewhat modified by the work of Thorpe, Ingold, and others, it still remains a brilliant and highly suggestive piece of theoretical work. The complete statement of this theory is set out in two and a half pages of print, and is indeed a marvel of concise and accurate expression, which may serve as a model for writers of papers of the present day to show how few words and how little space are often really necessary to make clear even so novel a theory as the "Spannungs Theorie" was at the time it was put forward.

Between the years 1884 and 1893, Baeyer published a mass of work of a very varied kind, including as it did the synthesis of hydrindene-carboxylic acid, tetrahydronaphthalenedicarboxylic acid, and naphthalene, a discussion of the synthesis of acetoacetic ester, the important synthesis of phloroglucinol by the action of heat on the sodium derivative of malonic ester, and the conversion of phloroglucinol into the trioxime, which showed for the first time that phloroglucinol may function both as trihydroxybenzene and triketo-hexamethylene.

These researches gave rise to the well-known series of investigations on the properties of succinylsuccinic ester and to the study of the conditions under which *p*-dihydroxyterephthalic ester changes into this ester, and thus evidence gradually accumulated which led Baeyer to draw the general conclusion that certain benzene derivatives, and the hydroxy-derivatives in particular, are in many cases, capable of being converted by tautomeric change into derivatives of hexahydrobenzene. The inquiry into the mechanism of these and other remarkable changes of the same character made it evident to Baeyer that the Kekulé formula for benzene did not satisfactorily account for the existence of such tautomeric modifications, and, as an alternative, he suggested the well-known centric formula for benzene which had also been put forward by Armstrong.

Another outcome of these researches was the discovery of a

simple method for the preparation of *p*-diketohexamethylene and of its conversion into *p*-dihydroxyhexamethylene (chinitol) and then into di-, tetra-, and hexa-hydrobenzene.

It was during the course of this epoch-making investigation that Baeyer first put forward the important generalisation that the distinctive aromatic character of benzene and its derivatives is entirely destroyed when the nucleus is reduced, and that substances like di-, tetra-, and hexa-hydrobenzene have no longer an aromatic character, but are essentially similar in properties to substances belonging to the aliphatic series.

This novel view of the character of the simple reduced benzenes, as well as other theoretical considerations which had emerged during the progress of the researches under review, suggested to Baeyer the desirability of taking up the systematic investigation of the reduction of benzene derivatives and especially the study of the reduction of the phthalic acids, a field of work already somewhat familiar to him on account of his earlier researches on the reduction of mellitic acid. It is impossible to give even a brief survey of these intricate investigations, which are so masterly in all their details that they must always remain as a monument to Baeyer's experimental skill and theoretical ability. It must suffice to mention the fact that the experiments on the reduction of terephthalic acid were so exhaustive that they resulted in the preparation and characterisation of every hydroterephthalic acid which would be expected to exist, if our theories of the structure of organic compounds are correct. This series of the reduction products of terephthalic acid consists of four dihydroterephthalic acids, one of which exists in *cis*- and *trans*-modifications, two tetrahydro-acids, one existing in *cis*- and *trans*-modifications, and one hexahydroterephthalic acid, which again exists in *cis*- and *trans*-modifications.

This remarkable agreement between experiment and theory is a striking illustration of the almost uncanny accuracy of the prevailing views of the structure of organic substances.

The reduction of the phthalic acids may be readily brought about by means of sodium amalgam, but the benzene hydrocarbons and many derivatives of benzene cannot be reduced by this process, and it was not until much later that the method of reduction by means of hydrogen in contact with nickel, discovered by Sabatier and Senderens, and the still more elegant process devised by Willstätter of reducing with hydrogen in the presence of specially prepared spongy platinum, removed this difficulty and amplified and extended the work of Baeyer.

In the course of the researches on succinylsuccinic ester, which occupied much of his attention during the years 1886-1893,

Baeyer showed that the methylisopropyl derivative of this ester is converted on hydrolysis and subsequent reduction into methylisopropylehinitol (methylisopropyl-dihydroxyhexamethylene), from which, by elimination of water, he was able to prepare methylisopropyl-dihydrobenzene, $C_{10}H_{16}$. He thus succeeded, with the aid of such simple materials as methyl alcohol, acetone, and succinic acid, in accomplishing the first synthesis of a terpene.

The discovery that this synthetical dihydrocymene, containing as it does the two double linkings in the nucleus, is not identical with any known terpene greatly surprised and interested Baeyer, and it is evident that it was the consideration of this fact which induced him to commence that long and brilliant series of investigations on the terpenes which shortly afterwards began to appear.

The results of this difficult work are contained in twenty-five communications to the *Berichte*, entitled "Ortsbestimmung in der Terpenreihe," and it is curious and worthy of note that all these papers, from the first, published in 1893, to the last, which appeared in 1899, are marked "Vorläufige Mittheilung." This course, not adopted in any other series of his researches, would seem to suggest, as indeed actually appears to have been the case, that Baeyer was never quite satisfied with the experimental results, and especially with the theoretical considerations deduced from them, and intended at a later date to put the whole subject matter together in the form of a pamphlet. This was, however, never done. The suggestion has been made that in certain respects, and especially from the point of view of theoretical insight and treatment, these researches are less brilliant and convincing than much that had gone before. The long paper, the fifth of the series, deals, among other matters, with the difficult problem of the constitution of dipentene and, in discussing this problem at length, it is certainly remarkable that Baeyer did not recognise or consider the possibility of the hydroxyl group in terpinol being situated in the isopropyl side-chain. The view that this hydroxyl group is situated in the partly reduced benzene nucleus caused Baeyer to assign to dipentene a constitutional formula which did not contain an asymmetrical carbon atom, and therefore did not account for the fact that dipentene is an externally compensated mixture of *d*- and *l*-limonenes. In order to overcome this difficulty, Baeyer was driven to the assumption that dipentene was the first exception to the Le Bel and van't Hoff generalisation, and that this generalisation required extension to meet cases of this kind, for he says: "The optical activity of limonene must be due to the asymmetry of the molecule as a whole, and does not depend on the presence of an asymmetric carbon atom in the sense of the doctrine of Le Bel and van't Hoff." This failure

to grasp the real character of dipentene caused a good deal of confusion at the time, which extended to other members of the terpene group, and was responsible for the incorrect formulæ which were at first assigned to carvestrene and sylvestrene. It was not until the famous theoretical paper of Wagner appeared in Russian in 1894, and terpineol had been synthesised in 1908 from Δ^1 -tetrahydro-*p*-toluic acid, that the nature of this substance can be said to have been clearly understood and its constitution established. In spite of the confusion connected with the constitution of limonene, the terpene researches of Baeyer contain a great amount of very accurate theoretical work of the highest importance. Very brilliant, for example, both from the experimental and the theoretical points of view, is the series of researches on the conversion of the naturally occurring ketone carvone into carone and the oxidation of the latter to caronic acid, which Baeyer obtained in *cis*- and *trans*-modifications and recognised as *gem*-dimethyltrimethylene-dicarboxylic acid. This remarkable and highly important acid, the constitution of which was subsequently confirmed by synthesis, was destined later on to play a great part in connexion with the discussion of the ease of formation, stability, and other properties of the trimethylene or cyclopropane ring. Baeyer, moreover, made the interesting observation that carone may be converted either into a derivative of *m*-cymene or into a derivative of *p*-cymene, according to the direction in which the *gem*-dimethyltrimethylene ring suffers scission. These experiments led, as is well known, to the discovery of carvestrene, which, on careful examination, proved to be the externally compensated modification of sylvestrene, and thus the important conclusion was drawn that this constituent of pine-needle oil is that derivative of *m*-cymene which corresponds to limonene in the *p*-series. Perhaps of still greater significance are the elaborate series of experiments which Baeyer carried out on the oxidation of pinene, since these furnish the proof, which at the time was wanting, that the Wagner formula for pinene, containing a *gem*-dimethylcyclobutane ring and one double linking in the reduced benzene nucleus, is the correct representation of the constitution of this most widely distributed of all terpenes. In the course of these difficult experiments, Baeyer isolated and characterised pinonic acid, pinic acid, and norpinic acid, a series of acids of more than ordinary interest on account of the fact that they all contain the *gem*-dimethylcyclobutane ring assumed by Wagner to exist in pinene. It is remarkable that, whilst nearly all the degradation products of the terpenes have now been prepared synthetically and their constitutions quite definitely established, all attempts to synthesise the *gem*-dimethylcyclobutane acids just

mentioned have so far been quite unavailing. During the course of these researches, Baeyer also discovered pinoylformic acid and nopinone, two substances of great interest which he recognised as being derived, not from pinene itself but from *isopinene* (nopinene), the isomeride which contains the double linking in the side-chain instead of in the ring, and is a constituent of most samples of commercial oil of turpentine.

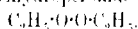
It was while engaged in researches in the terpene group that Baeyer first began to experiment with Caro's acid, a reagent which he found of the utmost value in the determination of the constitution of terpenes, and particularly of cyclic ketones of the terpene group. In 1898, Caro had discovered that a persulphate, when treated with concentrated sulphuric acid, is converted into a new acid which is a powerful oxidising agent, but differs from other acid oxidising agents in several important particulars. All attempts to isolate the new acid failed, but a long and very interesting examination of the properties of its solutions clearly proved that it is an oxidised sulphuric acid of the formula H_2SO_5 , and for this Baeyer suggested the name "Sulfomonopersaure."

This oxidising agent was first used by Baeyer with success in establishing the constitution of terpinolene, but subsequently he found that it was particularly valuable because of its specific action on ketones, which it converts into peroxides or in the case of cyclic ketones into lactones. On subsequent hydrolysis, these lactones yield the corresponding hydroxy-acids, and it is then only necessary to determine the constitution of the hydroxy-acid in order to be able to deduce the structure of the ketone from which it was derived.

Following on, and indeed in continuation of, the investigation of the oxidising action of Caro's acid, there began to appear in 1900, when Baeyer was sixty-five years of age, the brilliant series of researches on peroxides and oxonium salts. Perhaps one of the most remarkable features of these papers, all of which were published in conjunction with his assistant, Victor Villiger, and deal largely with problems connected with Inorganic Chemistry, is the large series of analytical methods which were developed in the determination of the constitution of Caro's acid and allied acids, as well as of the peroxides. It was, no doubt, a natural consequence of the discovery of the conversion of ketones into peroxides by the action of Caro's reagent (or a mixture of hydrogen peroxide and sulphuric acid, which answers the same purpose) that Baeyer should direct his attention to the general question of the formation and properties of peroxides. It is interesting in reading these papers to endeavour to follow the line of thought which led, from the first simple results, to so many developments in such a variety of directions, but this

is impossible on the present occasion, and all that can be attempted is to indicate quite briefly one or two of the more striking features. Benzoyl peroxide, $(C_6H_5CO)_2O_2$, is produced, as is well known, when benzoyl chloride reacts with barium peroxide, or with hydrogen peroxide in the presence of sodium hydroxide, and Baeyer found that this substance is hydrolysed by sodium ethoxide with the formation of the sodium salt of benzoyl hydrogen peroxide (benzopersäure), $C_6H_5COO\cdot OH$, which is, of course, a powerful oxidising agent. The discovery and examination of benzoyl hydrogen peroxide gave the explanation of the mechanism, which had for so long not been understood, of the ready oxidation of benzaldehyde by air. Baeyer showed that benzoyl hydrogen peroxide is first produced, and that this then reacts with a second molecule of benzaldehyde, yielding two molecules of benzoic acid.

Another very important development of this research was the discovery of the ethyl derivatives of hydrogen peroxide, $C_2H_5\cdot O\cdot OH$ and $C_2H_5\cdot O\cdot O\cdot C_2H_5$, produced by the action of ethyl sulphate on hydrogen peroxide in the presence of alkali. These substances are colourless liquids which distil at 65° and 95°, respectively; and the interesting observation was made that, whilst the former is a powerful oxidising agent, the latter is inert and resembles ether in its properties. That diethylhydroperoxide has the formula



derived from $H\cdot O\cdot O\cdot H$, and not $O\cdot O\cdot \begin{smallmatrix} C_2H_5 \\ C_2H_5 \end{smallmatrix}$, derived from $O\cdot O\cdot \begin{smallmatrix} H \\ H \end{smallmatrix}$,

is clearly shown by the observation that, on reduction with zinc dust and acetic acid, it yields two molecules of alcohol and not ether, as was to be expected if the second formula had been correct. Baeyer regarded this as strong evidence in favour of the formula $H\cdot O\cdot O\cdot H$ for hydrogen peroxide.

In the course of these experiments, Baeyer investigated with great care the action of silver oxide on hydrogen peroxide, and showed, from the accurate measurement of the amount of oxygen liberated, that the process takes place in a simple manner according to the equation $Ag_2O + H_2O_2 = 2Ag + H_2O + O_2$, whereas Berthelot had assumed that an oxide of silver, probably Ag_2O_3 , is first produced and then decomposes into silver and oxygen.

The experiments on benzoyl hydrogen peroxide, on the ethyl derivatives of hydrogen peroxide, and on the constitution of hydrogen peroxide caused Baeyer to direct his attention to the properties of oxygen in general and particularly to the question whether oxygen can or cannot function as a quadrivalent element. He became specially interested in the brilliant researches of Collie, who, in 1899, as the result of his investigation of the salts produced

by the combination of dimethylpyrone with acids, had not only put forward the view that oxygen can function as a quadrivalent element, but, what was still more striking and novel, that it can exhibit pronounced basic properties. That substances such as aurin, fluorescein, and other phthaleins yield salts with sulphuric acid had been known since 1876, and in 1896 A. G. Perkin described a whole series of salts which yellow colouring matters of the quercetin group yield with acids. As these colouring matters are derivatives of γ -pyrone, this observation, in view of the subsequent development of the subject, is of considerable historical interest, but, on the other hand, A. G. Perkin, in common with others who investigated salts of this kind, concluded that they are merely molecular compounds of the dyestuff and the acid. Collie and Tickle, however, as the result of their experiments on a great variety of salts of dimethylpyrone, drew the conclusion that the formation of these salts is due to the bridge oxygen in dimethylpyrone becoming quadrivalent and basic, just as the nitrogen atom in the pyridones and other nitrogen derivatives becomes quinquivalent and basic when it combines with acids. They therefore named these comparatively unstable oxygen salts "oxonium salts." Baeyer and the members of his staff were at first radically opposed to these views of Collie and Tickle, and especially to the suggestion that oxygen could assume basic properties. But, as the facts accumulated, Baeyer was gradually forced to change his attitude and ultimately he became a most enthusiastic supporter of the oxonium theory. In discussing this change of view, he says in one place: "But I am never obstinate, nor is it my habit to adhere to any view when I find that it no longer agrees with the facts." In order to examine the whole matter for himself, he commenced at the age of sixty-six, and again in collaboration with his friend and assistant, V. Villiger, the well-known and brilliant series of researches, "*Ueber die basischen Eigenschaften des Sauer-stoffs*," and it is remarkable, as illustrating his change of attitude, that on the second page of the first paper there occurs the subsection, "Proof of the fact that all classes of organic derivatives of oxygen possess basic properties." At a later date, Baeyer somewhat qualified this statement, and showed that the peroxides were an exception to this generalization, since they proved to be incapable of yielding oxonium salts. In connexion with these researches on the basic nature of oxygen, Baeyer became much interested in the basic properties of carbon. The incentive to these researches, which belong to the last period of his activities, was the observation that triphenylcarbinol dissolves in sulphuric acid, yielding a yellow solution of a salt, which, however, on the addition of water, is dissociated with separation of the carbinol.

In the case of tri-*p*-anisylcarbinol, the basic nature becomes so much more pronounced that this substance is capable of forming salts even with dilute acids. Considerable controversy arose as to the explanation of this remarkable state of things. Kehrman was of the opinion that, in the formation of the coloured salts of the triphenylcarbinols, one of the benzene rings became quinonoid, yielding salts of the type $\begin{matrix} \text{C}_6\text{H}_5 \\ \text{C}_6\text{H}_5 \end{matrix} > \text{C}^+ < \begin{matrix} \text{CH}_2\text{CH} \\ \text{CH}_2\text{CH} \end{matrix} > \text{C}^+ < \begin{matrix} \text{H} \\ \text{Cl} \end{matrix}$. Baeyer, on the other hand, preferred to represent such salts, as, for example, triphenylmethylsulphate, as $(\text{C}_6\text{H}_5)_3\text{C}^+ \cdot \text{O} \cdot \text{SO}_3\text{H}$, the curved line, called by him the carbonium linking, indicating the particular valency which is capable of combining with the acid radicle. It would appear that the constitution of these curious salts remains to the present day an open question.

Baeyer continued right to the end to interest himself in the oxonium salts of the pyrone type, and his last research, published in 1915 (*Lundén*, 407, 322), when he was eighty years of age, has for its subject the reduction of the pyrones. This communication contains the first description of the oxonium colouring matters, substances of great interest particularly because of the probability that they are allied to colouring matters which Willstätter has isolated from the blood and from plants; and this brilliant piece of theoretical and experimental work shows that Baeyer retained his great powers as a thinker and investigator to the last. It is highly probable that he would still have continued his researches but for the fact that, when all his assistants had been called away to the war, he felt unable to carry on quite alone.

In attempting to pass in review the life and career of a great personality such as Baeyer unquestionably was, the mere discussion of his published researches can at the best give only a very inadequate impression of the real character of the man. And yet, on account of his retiring nature and dislike for publicity, and also because he travelled little in other countries, the actual man was known to comparatively few, and it is not easy to convey a clear impression of the personal traits which were his characteristics. Probably the most distinctive feature in Baeyer's character was the steadfastness of purpose and determination to allow nothing to interfere with his duties as a teacher or with the course and development of his investigations. He made it quite clear to the University authorities that he would have nothing to do with general University politics and he always refused to serve on committees or attend meetings unless they were directly concerned with the affairs of his department. He felt strongly that it was his business

and duty to have no part in any outside work, unless it was absolutely unavoidable, which took him away from his laboratory. He would have been horrified at the waste of time and energy, due to attendance at committees and other meetings, which would seem to be an essential part of the routine of heads of Chemical Departments in this country.

There can be no doubt that it was this refusal to waste time, coupled with his extraordinary power of concentration, which made it possible for Baeyer to produce, with such regularity, so great an amount of work always full of originality and of first-rate importance. Another reason for the enormous output of original work is to be found in the fact that he regulated his whole life so that nothing should stand in the way of the development of his researches.

During term time, he lived with his family in the fine house attached to the laboratory, and had only to go along a corridor to get to his private laboratory. He took little exercise, and was of the opinion that exercise, other than that involved in the daily occupation, was not essential to health. He seldom attended the theatre and was not interested in music, for the author well remembers how bored he was on one occasion when his assistant Homolka—a great Wagner enthusiast—persuaded him to sit through a five-hour performance of the "Götterdämmerung." About the year 1895 he purchased an estate, consisting of a fine house, which he called "Villa Baeyer," situated in a large and beautifully wooded park on the shores of the lake of Starnberg, and it was a great delight to him to stroll among the trees and enjoy the beautiful scenery. It was here that he died on August 20th, 1917.

Baeyer was accustomed to take good holidays, and, in the early Munich days, it was his wont to spend Easter or the late autumn in the Tyrol, usually at Gries near Bozen, but on other occasions he paid frequent visits to other beautiful spots in the Bavarian Highlands.

One rather unexpected feature of Baeyer's character was the pleasure he took in the ordinary routine of lecturing and he used to say that he felt the day had not been really a satisfactory one if he had not given his usual lecture in the morning. As a lecturer, Baeyer was most interesting and clear: he spoke quietly, without hesitation and in a level tone throughout, and without any attempt at oratorical effect. The lectures were always attractive, partly on account of their severely elementary nature and partly, perhaps, because of the original manner in which everything was treated, the impression conveyed being that he was considering the subject from new points of view while he was actually delivering the lecture. It is unfortunate that Baeyer seldom lectured on any but the most

elementary matters, and rarely indeed gave to his students or colleagues any account of his own investigations or of the lines on which he proposed to proceed in the development of the researches he had in hand.

In attempting to convey some idea of his methods of research, the fact must again be emphasised that Baeyer was a great reader, especially of current literature, and the remarkably wide and thorough knowledge he had of the literature of the subjects he was interested in is obvious from the clear, concise, and complete way in which the introductions to his papers are written. Before deciding on the next line of action and as a preliminary to starting the experimental investigation of any problem, it was usual for him to walk slowly up and down in his study, or more frequently in his laboratory, turning things over in his mind; he never seemed to be in a hurry, and, so far as the author remembers, he seldom made notes, and it was not his habit to cover sheets of paper with formulæ.

His private laboratory, in which the author had the good fortune to work for a year, was equipped with the simplest possible apparatus, the most striking feature being large racks, such as are commonly in use at the present time, filled with test-tubes. He insisted always on absolute cleanliness, and it used to be said that his test-tubes were first soaked in dilute caustic soda for an hour, then washed with water, then with alcohol, and finally with distilled water and dried.

Baeyer also used large numbers of carefully cleaned glass rods and had always a stock of these to hand, placed upright in wide-mouthed bottles; there were also small flasks, beakers, etc., but the striking feature of the laboratory was the absence of any large apparatus as well as of mechanical devices of any kind.

Directly he came into the laboratory, Baeyer used to have a short preliminary talk with his assistant, in the course of which he would examine any substances which the latter had prepared during the previous day. He would then begin to investigate the new material by subjecting it to a searching series of test-tube experiments, and, as the result of long practice and experience, he seemed to know intuitively what kind of treatment was most likely to lead to the result he desired. Baeyer had what may be described as the chemical instinct in a remarkable degree, and almost seemed to know beforehand what was going to take place. But it nevertheless sometimes happened that whole days or even weeks of experimenting produced nothing of any importance. The story is told of one period of six months during which, in spite of persistent experimenting, no results of any value were obtained, but the problem did not on this account cease to interest Baeyer,

and one day he came into the general research laboratory to show a wonderful test-tube experiment which had completely changed the outlook and supplied the explanation for the long series of failures. After this difficulty had been overcome, the whole investigation progressed by leaps and bounds, but no one reading the published paper can have any idea of the labour and patience which were necessary before the end was achieved.

Baeyer used to say that the only way to tackle a problem was to keep on experimenting until it was solved, and Willstätter relates that, on one occasion, a colleague from another University, whilst congratulating Baeyer on a great piece of work he had just finished, remarked that he only wished that such luck would come his way. To which Baeyer replied: "It is not a matter of luck. I have no more luck than you have. The only difference between us is that I experiment more than you do." When any test-tube experiment had given a result which was thought to be of sufficient importance, Baeyer used to repeat it and show it to his assistant, and the latter was then left to carry out the work on a somewhat larger scale, so as to provide the material necessary for further developments. Even then everything was always done on quite a small scale, and probably no chemist ever achieved so much and obtained such brilliant results with the expenditure of so little material.

The attitude of Baeyer towards experimenting may be expressed in his own words: "I do not make the experiment in order to see whether my views are or are not correct, but in order to find out what the behaviour of the substance is under a variety of conditions. It is for this reason that I attach little importance to theories." It is true that Baeyer was essentially the experimenter and was by disposition not greatly interested in theoretical matters. He had no liking for the method of working out a theory on paper and then going into the laboratory to see whether the ideas were right or wrong—his plan was to work out the theory from his experiments, and usually not until the experimental material was practically complete. When any new development had arisen, it was his custom to discuss its theoretical bearing with the seniors in the laboratory, and in writing up his papers for publication he always spent a great amount of time in elaborating the theoretical introduction.

The reader of these papers cannot fail to be struck by the brevity with which everything is related: probably no investigator ever described his results and their theoretical bearing in so few words. Although always concise and clear, the descriptions of the experimental conditions erred, perhaps, in not a few cases, in being too brief, and some of us, who have had occasion to repeat his results,

would have had an easier time and been thankful if the directions had been somewhat more detailed.

The one side of theoretical Organic Chemistry which interested him more than any other was the structural aspect, and the study of the introductions to his papers shows how remarkably accurate were his notions of structure even in early times. It was doubtless this interest in structural formulæ which led to the enunciation of the "Spannungs Theorie," and to his views on the structure of benzene.

Perhaps for the reason that he was accustomed to do all the experimental work himself, Baeyer had little inclination to work with others, and the titles of his papers show that, whilst he frequently published with one or other of his assistants—to a greater extent with Victor Villiger than with any of the others—the actual number of his co-workers was relatively small. This is the more surprising when it is remembered that the laboratory was always overcrowded with the most promising material from all parts of the world, and that every new-comer would have considered it a great honour to have been allowed to work with the head of the laboratory. Neither did Baeyer often suggest subjects for the researches which so many of the younger men were carrying out for their dissertations for the Ph.D. degree. When the time came to do original work, these young researchers were usually handed over to one of the many Privatdozenten attached to the laboratory, and it was the duty of these senior men, who were often men of great experience, to suggest the theme for investigation and to superintend the work and help to bring it to a satisfactory conclusion. This plan worked well, and gradually there rose up a great school of research which has rarely if ever been equalled. It used to be said that, at one time, almost every Professor of Organic Chemistry of eminence in Germany was a pupil of Baeyer, and it is equally certain that the great majority of the leading figures in the Organic Chemical Industry learnt their methods of research in the Munich laboratories.

It was, however, the example Baeyer himself set which was the driving force and the mainspring of the great reputation which the Munich School enjoyed and still enjoys under his distinguished successor. There was a feeling in the laboratory that no one was of any account who did not research, and, moreover, the position of each researcher and the esteem in which he was held depended solely on the quality of the work he was engaged in. This was the atmosphere which produced the greatest chemists of the day and weeded out those who were of no account. It was only necessary that the commanding figure of Baeyer should stroll through the

research laboratories each day and for him to chat with the various workers, criticise their results, and admire their preparations, to make it out of the question for anyone to forget for a moment that research was the only thing that really mattered. It is impossible not to be struck by the fact that this same attitude has, since the war, become increasingly evident in the laboratories in our own country, and that research has now come to be looked upon as a most important, if not the most important, part of the training and education of every chemist.

Baeyer married, in 1868, Lida, daughter of Geheimrat Bendemann of Berlin, who died in 1910, and there were four children, a daughter and three sons.

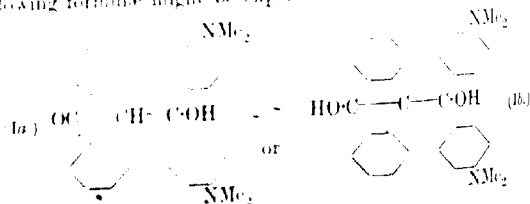
The daughter, Eugenie, married Oscar Piloty, who became extraordinary Professor of Chemistry in Munich and fell in the war in 1915; of the two surviving sons, Hans (born in 1875) is Professor of Orthopaedic Surgery in Heidelberg and Otto (born in 1877) is Professor of Physics in the Landwirtschaftliche Hochschule in Berlin.

CLXXIII.—*The Preparation and Properties of 4':4''-Tetramethyldiaminoanthrafuchsone.*

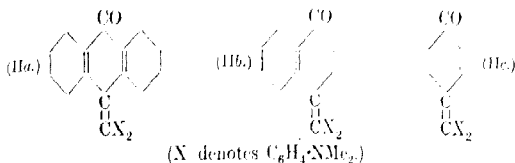
By FREDERICK ALFRED MASON.

THE condensation of Michler's ketone (*pp'*-tetramethyldiaminobenzophenone) with anthrone is of interest because, although a large number of important dyes have been prepared by condensing the ketone with various benzene and naphthalene derivatives (for example, Victoria Blue-B, Wood Green-S, etc.), there are no known dyes obtained by the condensation of this ketone with anthracene derivatives. Padova (*Ann. Chem.*, 1910, [viii], **19**, 389) attempted to condense anthrone ("anthranol") with Michler's ketone, but only managed to obtain a few red crystals melting indistinctly at 260–270°.

On condensing together the two substances in presence of phenyl chloride, the formation of a carbinol having one of the following formulae might be expected:



When molecular amounts of the above reagents are heated together in benzene solution for twenty hours, a product is finally obtained which, after purification as described in the experimental part, forms bright brick-red crystals melting at 264–265° and analyses correctly for a substance of the formula $C_{31}H_{28}ON_2$. It therefore have the structure indicated in formula (IIa).



Its systematic name is accordingly either 4':4''-tetramethyl-diaminodiphenylmethylanthrone, 4':4''-tetramethyldiaminodiphenyl-9:10-anthraquinomethane, or 4':4''-tetramethyldiamino-anthraquinone, and it is probably identical with the "crystaux rouges" of Padova (*loc. cit.*).

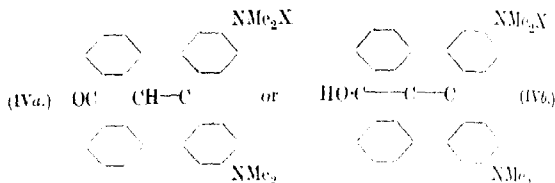
It is a derivative of the parent substance diphenylanthraquinomethane, $C_6H_5\langle\begin{smallmatrix} CO \\ \diagup \diagdown \\ CPh_2 \end{smallmatrix}\rangle C_6H_5$ (II), obtained by Padova (*Compt. rend.*, 1906, **143**, 121) by condensing benzophenone chloride with anthrone, which is stated to be colourless though forming coloured solutions.

The red substance (IIa) is obviously formed from the corresponding carbinol (I) by loss of a molecule of water and will for this reason be termed the "anhydro-base." It is of special interest in that it completes the series of quinonoid bases of which the naphthalene and benzene analogues have already been made by Noelting and Saas (*Ber.*, 1913, **46**, 952) and by Schlenk (*Annalen*, 1909, **368**, 291) respectively, namely, tetramethyldiaminonaphthafuchsone and tetramethyldiaminofuchsone (formulae IIb and IIc), and its properties, though somewhat unexpected at first sight, will be found to agree generally with what might be expected for the extreme of such a series.

The bright brick-red crystals of the new "anhydro-base" are only very sparingly soluble in most neutral solvents such as alcohol, tetrachloromethane, toluene, and benzene, in which they dissolve to deep brown solutions. Attempts to prepare the phenylhydrazone were unsuccessful. The anhydro-base does not form a "vat" and remains unchanged even after heating for some time with alkaline hyposulphite solution.

It dissolves readily in glacial acetic acid or in alcohol containing the calculated amount of hydrochloric acid, to give intense blue

solutions of the salts of a dye which may be termed *Anthranol Blue* (compare the "Naphthol Blue" of Noelting and Süss) which must presumably have one of the following constitutions:



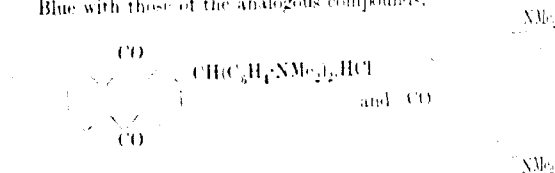
For reasons which will be referred to later it is believed that formula (IVb), corresponding to the endic form of anthrone (anthranol), is the more probable.

The table on p. 1549 compares some of the chief properties of tetramethyldiaminofuchson (A), tetramethyldiaminonaphthafuchson (B), and tetramethyldiaminoanthrafuchson (C).

Perhaps the chief distinction between (B) and (C), apart from the actual colour of the salts, is that the naphthafuchson derivative is very easily hydrated to the ammonium base, for example, the solution in dry pyridine is brownish-red, which becomes blue-violet on adding water (conversely the blue-violet solution of the ammonium base becomes red on boiling for a few minutes), whilst the anthrafuchson-ammonium (or imonium) base is quite unstable and loses water, even on washing with cold alcohol, to give back the anthrafuchson base itself.

In passing it may be noted that an examination of the naphthas- and anthra-fuchson derivatives suggests that the intense "magenta red" alcoholic solution of the tetramethyldiaminofuchson obtained by Schlenk (*loc. cit.*) may be really a solution of the corresponding imonium base (formula Vb) and not of the actual fuchson derivative itself.

It is of interest also to compare the colour of the salts of Anthranol Blue with those of the analogous compounds,



the former having been prepared by Ullmann and Kligenzweig by the action of anthraquinonealdehyde on dimethylamine (*Ber.*, 1915)

Colour of solution in

	M. p.	Colour.	Benzene.	Abs. alcohol.	Aqu. alcohol.	Abs. pyridine.	Aqu. pyridine.	Colour of salts in alcohol.	Colour of ammonium base.
<i>Al.</i> ^{2,3}	—	Black-red ¹	Orange-red ¹	Magenta (?) ¹	Magenta (?)	—	—	Intense green ²	Reddish-violet ²
<i>B</i> ^{4,5}	266-270	Deep coloured prisms ^{4,6}	Brownish- red ^{4,5}	Purplish- red ⁵	Purplish- blue ⁵	Red ⁵	Purplish- blue ⁵	Intense purplish- blue ⁵	Purplish-black (stable in alcohol) ⁵
<i>C</i>	264-265	Black-red	Deep brown	Reddish- brown	Deep purple	Dirty brown	Purple	Intense greenish- blue	Purplish-black (decomposed by cold alcohol to give C)

¹ Schlenk, *loc. cit.*² O. Fischer, *Ber.*, 1881, **14**, 2322.³ Compare Volcock and Jackson, *Proc.*, 1907, **40**, 406. (The product obtained by V. and J. from Michler's hydrof and anisole must probably have lost the methyl of the methoxyl group under the conditions of their experiments. F. A. M.)⁴ Noeding and Sauer, *loc. cit.*⁵ Independent observations (F. A. M.).⁶ The crystals as they first separate out from benzene solution are deep orange-brown, but become almost opaque and deeply coloured when cold (F. A. M.).

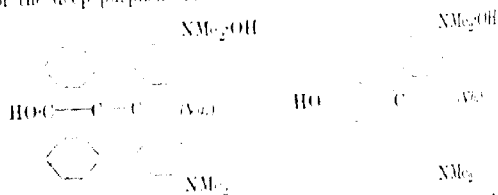
46, 713) and having a yellowish-green malachite-green shade, whilst the latter (*s*-tetramethyldiaminodiphenylanthrone) forms well-crystallised, colourless salts.

The basic properties of the carbinol base of Anthranol Blue are, however, so remarkably weak that its salts are at once completely hydrolysed by water. The sensitiveness of the blue salts to water may be seen if a piece of filter-paper is soaked in an alcoholic solution of the intensely blue hydrochloride and then a drop of water allowed to fall on the dry paper. A black spot is immediately produced, due to the hydrolysis of the salt.

The coloured hydrochloride may be obtained with some difficulty in a crystalline form by treating the base with the calculated quantity of alcoholic hydrochloric acid and allowing the solution to evaporate slowly in a desiccator. The hydrochloride forms bronzed-purple leaflets which decompose readily on exposure to air. If excess of hydrochloric acid be used, the yellow diacid salt will be precipitated, which rapidly turns bluish-green in the air owing to incipient hydrolysis. The same series of changes may be observed on passing a current of dry hydrogen chloride into a solution of the anhydro-base in hot toluene.

As mentioned above, the salts are immediately hydrolysed by water; on diluting the alcoholic solution of the hydrochloride with water, the intensely blue solution becomes first bluish-purple, then purplish-black, and finally a black precipitate separates, which is also formed when the alcoholic or acetic acid solution is poured into dilute alkali. When filtered off and pressed on a porous plate, it forms a deep black powder which, on leaving in a vacuum desiccator, warming on a water-bath, or even washing with cold 95 per cent. alcohol, is immediately reconverted into the red anhydro-base by loss of a molecule of water.

Of the possible formulae for this purplish-black substance, the following (Va) appears to be the most probable and would account for the deep purplish-black colour:



This formula represents the purplish-black substance as the free ammonium or rather imonium base corresponding to the salts (IV), and this view would agree with the similarity in colour of

this free base with the base from the benzoic ester described below, which can only have a formula analogous to (Va). Further it would agree with the observation of Noeltting and Saas, who obtained the free coloured ammonium base from hexamethyltriaminodiphenyl-naphthylcarbinol (*loc. cit.*).

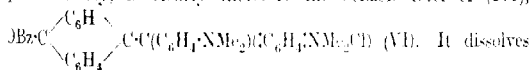
It has not been found possible to purify the base for analysis owing to its instability.

On account of the unexpectedly weakly basic character of the dye base, the salts are obviously of no use as colouring matters. This lack of stability was thought to be due to the well-known tendency of the anthraquinone portion of the molecule to revert to the quinonoid or keto-form. If, therefore, the enolic form could be "fixed" by alkylation or esterification it was thought that the products might be more stable and have useful tinctorial properties.

It has not been found possible to alkylate the base with any of the usual alkylating agents such as ethyl bromide, benzyl chloride, methyl sulphate, or toluenesulphonic ester, although there are some indications of the formation of blue products.

Action of Benzoyl Chloride on the Anhydro-base.

More definite results are obtained by the use of acylating agents, in particular benzoyl chloride and its derivatives. On heating equal molecular amounts of the red anhydro-base and benzoyl chloride on the water-bath, the mass gradually becomes an intense purple with a metallic lustre, and the product crystallises from hot water (in which it is slightly soluble to a deep blue solution) as a greenish-yellow, bronzed metallic-looking powder, m. p. 192–194° (with decomposition). The product, which is formed almost quantitatively, is clearly therefore the benzoic ester of (IVb),



It dissolves readily in alcohol to an intensely blue solution which is practically identical in shade with that of the hydrochloride derived from the anhydro-base, so that this similarity in colour is a strong argument for the "enolic" formula (IVb) suggested for the salt.

The substance crystallises from aqueous solution with one molecule of water. The deep blue aqueous solution of the benzoic ester chloride dyes silk, wool, and tannin-mordanted cotton a bright greenish shade of blue, silk showing the most affinity for the dye, whilst tannined cotton has rather poor affinity. The dyings darken, however, on prolonged boiling owing to gradual hydrolysis, with formation of the violet-black imonium base (Va). Addition of sodium carbonate to the blue solution changes it gradually to

purple, and violet-black flocks are precipitated, the blue colour being restored by dilute acetic acid. Boiling the solution of the benzoic ester chloride with a trace of acid, or even prolonged standing in the cold effects a gradual hydrolysis of the substance.

Action of Acetyl Chloride.

On treating a portion of the anhydro-base with acetyl chloride, a deep bronzed blue mass is formed which gives a blue solution in alcohol. On pouring into water, however, it is at once decomposed to the purplish-black imonium base and hence is not the acetic ester chloride sought: this can, however, be obtained in good yield by heating the anhydro-base with pyridine and acetyl chloride at 80–100° for eight to ten hours, and recrystallising the product from hot water: it forms brilliant, red, metallic leaflets which become purplish-blue on powdering and melt at 240–242° with decomposition.

This product must therefore be the chloride of the acetic ester, $\text{OAc} \cdot \text{C}_6\text{H}_4 \cdot \text{C}(\text{C}_6\text{H}_4 \cdot \text{NMe}_2)(\text{C}_6\text{H}_4 \cdot \text{NMe}_2\text{Cl})$ (VII); this deduction is confirmed by the analytical figures.

The acetic ester chloride is more readily soluble in water than the benzoate, but gives an identically coloured solution and dyes silk, wool, and tannin-mordanted cotton similar shades. Its affinity for silk is, however, less than that of the benzoate, and the bath does not exhaust so well, but the affinity for tanned cotton is rather better.

Behaviour with Acetic Anhydride.

When the anhydro-base is treated with acetic anhydride, it partly dissolves to a deep brown solution. After standing for some days the liquid becomes deep blue and on pouring into water a blue solution is formed, showing that acetylation has occurred to some extent. It has not, however, been found possible to obtain the acetate of the acetic ester by this means, as the greater part of the anhydro-base crystallises out unchanged, whilst a deep-seated decomposition occurs on prolonged heating. Noelling and Sias showed that in the case of the analogous naphthalene base acetic anhydride readily converted this base into the acetate of the green acetyl dye.

It may be mentioned that attempts to prepare the acetyl ester by direct condensation of Michler's ketone with acetylanthranol in presence of phosphoryl chloride gave negative results, the product

being a green syrup which contained much unchanged ketone and with no sign of the characteristic blue dye.

Behaviour with Other Acid Chlorides.

The anhydro-base reacts readily with *p*-nitrobenzoyl chloride and with toluene-*p*-sulphonyl chloride, giving in each case purplish-black products with metallic reflex which dissolve in alcohol to the intensely blue solution characteristic of Anthranol Blue and its ester salts. They are, however, even less soluble in water than the benzoate, the toluenesulphonic derivative being completely insoluble, and hence they are useless as colouring matters.

Action of Amines.

When purifying the anhydro-base by dissolving the crude substance in 75 per cent. alcohol with a slight excess of hydrochloric acid and then adding dilute ammonia, it is found that if an excess of the latter be used the yield of the anhydro-base recovered will be poor and the mother-liquor will have a purplish or greenish-black colour. On distilling off the alcohol, a black residue is left which dissolves in acetic acid to the characteristic deep blue solution and which, when heated with 10 per cent. caustic soda solution, evolves ammonia. The product has not been obtained in a pure form, but it appears probable that it contains the imino-ammonium base in which the group CO of formula (IVa) is replaced by C=NH (X being hydroxyl).

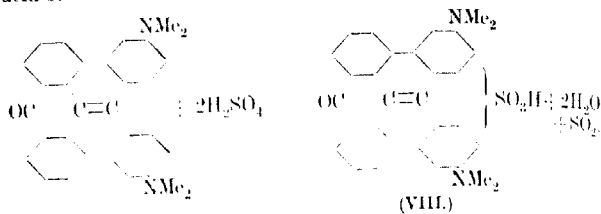
Attempts were made to prepare the analogue of crystal-violet in which the -C·OH group of formula (Ib) is replaced by -C·N(CH₃)₂. On heating the anhydro-base with alcoholic dimethylamine for some hours, however, most of the base was recovered unchanged, whilst further heating led to decomposition. In this respect the behaviour of the anhydro-base is identical with that of Noetting and Saas's naphthafuchsone derivative (*loc. cit.*, p. 961). On heating the anhydro-base with aniline, a blackish-brown product is obtained which is probably a decomposition product.

Action of Sulphuric Acid on the Anhydro-base.

With a view to determine whether soluble acid dyes could be obtained, the action of sulphuric acid has been tried on the anhydro-base and also on the benzoic ester chloride.

In the former case, it is found that ordinary sulphuric acid has little action even when heated. If, however, oleum is used, the initially brown solution becomes orange on warming on the water-bath, with an intense yellow fluorescence. As an odour of sulphur dioxide is noticeable during the reaction, it is probable that an

oxidation occurs leading to the formation of a complex benzanthrone derivative, which would explain the intense fluorescence in sulphuric acid solution which is characteristic of this class of substances :



The acid sodium salt of the resulting product gives a fairly deep red solution on dissolution in water and addition of sodium acetate or alkali, but it is in no sense of the word a dye.

Action of Sulphuric Acid on the Benzoic Ester Chloride.

The action of sulphuric acid on the benzoic ester chloride (formula VI) depends chiefly on the strength of the acid.

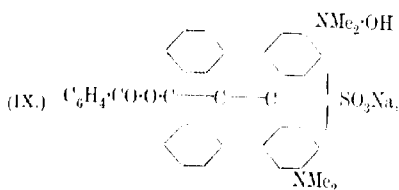
(a) On treating a portion of the substance with an excess of rather more than 100 per cent. sulphuric acid and leaving for a day, on pouring into brine a greenish-blue precipitate is obtained which dissolves in alcohol to the deep blue characteristic of Anthranol Blue; on adding alkali to the cold solution, red needles of the anhydro-base are at once formed, hence the greenish-blue precipitate is the acid sulphate of Anthranol Blue itself, the benzoyl group having been removed by hydrolysis by the acid.

(b) Prolonged treatment of the benzoic ester chloride with more concentrated oleum in the cold leads to the formation of a different substance which forms red salts, dissolving to deep red solutions in water which are decolorized by dilute acetic acid. It appears to be identical with the sulphonated product obtained from the anhydro-base itself, and dissolves in concentrated sulphuric acid to an orange solution with yellow fluorescence.

(c) If the benzoic ester chloride be treated with more concentrated oleum, warmed gently, and the product poured into ice and brine, a green precipitate will be obtained which is the acid sulphate of a sulphonic acid of the benzoic ester. It has the character of an indicator, as it dissolves in alkalis to an intensely purple-blue solution, which is turned deep greenish-blue by acetic acid and is practically decolorized by strong acids. It is capable of dyeing silk, but the dyings are similarly affected by acids and alkalis, so that it has no value as a colouring matter.

•This colour change is of interest in relation to the structure of

the unsulphonated dye, as it indicates that the purple-blue product obtained with alkalis is probably the soluble sulphonate of the imonium base,



corresponding to the purplish-blue but insoluble bases obtained from Anthranol Blue and from its benzoic ester, and the colour change, though pronounced, is hardly sufficient to support the view that the normal salts and the free base have different constitutions (compare Willstätter, *Ber.*, 1908, **41**, 1459).

Attempts have been made to prepare the benzanthrone derivative from the anhydro-base by heating the substance with glycerol and aniline sulphate in sulphuric acid, but no definite product has been isolated so far beyond a black, amorphous product which, in concentrated sulphuric acid, gives a brownish-pink solution with a pronounced green fluorescence.

The deep blue solution of Anthranol Blue in glacial acetic acid is decolorised by zinc dust after heating for some time on the water-bath, and on pouring into sodium carbonate solution a yellow precipitate is formed which is presumably the normal leuco-base, but has not been further examined.

EXPERIMENTAL.

4' : 4''-Tetramethyldiaminoanthracenone (Anhydro-base. Formula IIa).—The best method for preparing this substance is as follows:

Michler's ketone (54 grams; 1.5 gram-mol.) was dissolved in hot benzene (100 c.c.), phosphoryl chloride (33 grams) run in, and the whole kept for three hours. Recrystallised anthrone (39 grams) in benzene (100 c.c.) was then added and the mixture heated under reflux on the water-bath for twenty hours. The upper layer of hot, green benzene (containing some unchanged anthrone) was poured off and the residual cake of dark green, friable product broken up and dried in air, the weight of crude product being about 110 grams. Twenty grams of the powdered product were heated with water (200 c.c.) to 90° to decompose any unchanged ketochloride and dissociate any acid salt of the base, which is only sparingly soluble in alcohol. The mass frothed up slowly and became purplish-black. Alcohol (400 c.c. of 95 per cent.) was then

added and the whole boiled and filtered and the filtrate treated with 17 c.c. of 25 per cent. caustic soda solution. The deep blue liquid changed its colour to greenish-brown and deposited a fairly heavy reddish-brown precipitate of the anhydro-base, which was filtered off hot and washed with warm alcohol, pressed, and dried. Weight 10 grams. On this basis, the total yield was 55 grams (62 per cent. of theory).

The anhydro-base may be purified by crystallisation from 70 per cent. aqueous pyridine or, better, by solution in about 20 parts of 70 per cent. alcohol containing a slight excess of hydrochloric acid and then adding the calculated amount of alkali (ammonia or caustic soda) to the hot liquid, the pure anhydro-base separating out in bright red needles, m. p. 264–265°.

Attempts to improve the yield by adding phosphoryl chloride to the solution of Michler's ketone and anthrone during several hours gave only a 20 per cent. yield, much of the oxychloride being used up, apparently, by the anthrone (Found: C = 83.82; H = 5.97; N = 6.29. $C_{31}H_{28}ON_2$ requires C = 83.80; H = 6.36; N = 6.32 per cent.).

Acid Hydrochloride.—Five grams of the anhydro-base were suspended in hot toluene (100 c.c.) and dry hydrogen chloride was passed in. The deep bronze precipitate first formed became pale yellow with excess of acid and was quickly filtered off and dried over sulphuric acid (Found: Cl = 13.0. $C_{31}H_{28}ON_2 \cdot 2HCl$ requires Cl = 13.7 per cent.). The slightly low figure is probably due to incipient decomposition of the salt whilst weighing, as it immediately begins to hydrolyse in moist air.

Benzoin Ester Chloride (VI).—To a mixture of 8.8 grams of the anhydro-base and 10 c.c. of benzene, a solution of benzoyl chloride (25 c.c.) in benzene (10 c.c.) was added. The mixture was heated on a water-bath with occasional stirring for two hours, the product gradually becoming a fine purplish-bronze. After cooling, the cake was removed, ground, treated with benzene (10 c.c.) and benzoyl chloride ($\frac{1}{2}$ c.c.), and again heated on the water-bath for two to three hours. The weight of crude product was 11.8 grams (98 per cent. of theory).

The powdered product was purified by dissolving in 700 c.c. of hot water and filtering; after standing for a day, the bronze-yellow crystalline precipitate was filtered off and dried. (On one occasion the solution did not deposit crystals on cooling, but set to a thick, blue jelly; on warming, adding a few drops of concentrated hydrochloric acid, and cooling, the liquid deposited crystals in the usual way, leaving an almost colourless mother-liquor.) A suspension or solution of the substance gradually hydrolyses on standing, or

more rapidly on boiling (Found: C = 75.65, 75.74; H = 5.85, 5.66; N = 4.18; Cl = 5.69. $C_{33}H_{33}O_2N_2Cl \cdot H_2O$ requires C = 75.7; H = 5.82; N = 4.64; Cl = 5.88 per cent.).

Acetic Ester Chloride (VII).—To 4.4 grams of the anhydro-base, moistened with benzene (5 c.c.), pyridine (2 c.c.) was added and then a solution of acetyl chloride (1 c.c.) in benzene (5 c.c.). The mixture was stirred on the water-bath until nearly dry. A further quantity of benzene, pyridine, and acetyl chloride was added and the stirring and heating continued for eight to ten hours until the product was a purple-red, crumbly mass, which weighed 5.5 grams (practically theoretical). After powdering, it was recrystallised from hot water, in which it is somewhat more soluble than the benzoyl chloride derivative. It dissolves easily in alcohol, and melts and decomposes at 240–242° (Found: C = 74.38, 75.47; H = 5.93, 5.88; Cl = 6.79; N = 4.98. $C_{33}H_{31}O_2N_2Cl$ requires C = 75.75; H = 5.94; Cl = 6.78; N = 5.36 per cent.).

p-Nitrobenzoyl Ester Chloride and Toluene-p-sulphonyl Ester Chloride.—These products are formed readily by merely mixing together the calculated quantities of the anhydro-base and the acid chloride with a few c.c. of benzene, evaporating off the benzene, and keeping the mass molten for five to ten minutes. The *p-nitrobenzoyl chloride* derivative can be crystallised with difficulty from a large volume of water, and melts at 186–188° with decomposition.

The *toluene-p-sulphonyl* derivative has not been obtained in a pure form. Both derivatives are easily soluble in alcohol to the characteristic deep blue solution of Anthranol Blue and its derivatives.

Sulphonation of the Anhydro-base.—2.2 Grams of the anhydro-base were dissolved in 20 per cent. oleum (10 c.c.) to a green solution, which was then heated on the water-bath for a quarter of an hour until it was a clear brown with an intense yellow fluorescence. The liquid was poured on to a small amount of ice and saturated brine, and then saturated sodium carbonate added until the colour change from bluish-purple to purplish-red was complete. After standing, the bluish-red, metallic-looking precipitate was filtered off. It dissolves in water to a deep red solution which is decolorised by acids. It probably has the composition indicated by formula VIII.

The almost colourless acid salt was obtained by pouring the acid solution into brine and filtering off the crystalline precipitate of the sodium salt.

Action of Sulphuric Acid upon the Benzoyl Ester Chloride.—As already noted, sulphuric acid and oleum may act in one of three ways:

(a) *Hydrolysis of the benzoyl group.* 2.2 Grams of the benzoic ester chloride were added to an ice-cold mixture of 96 per cent. sulphuric acid (10 c.c.) and 20 per cent. oleum (2 c.c.), the brown solution was kept for a day and was then poured into saturated brine. A green precipitate was formed which was easily recognised as the acid sulphate of Anthranol Blue itself, as it gave a deep blue solution in alcohol and on adding alcoholic potash in the cold red needles of the anhydro-base were at once formed. The benzoyl group was therefore hydrolysed, but no sulphonation had been effected.

(b) *Hydrolysis and sulphonation.* 2.2 Grams of the benzoic ester chloride were added to an ice-cold mixture of 96 per cent. sulphuric acid (2 c.c.) and 20 per cent. oleum (10 c.c.), the product warming slightly. After standing two days, the mixture was poured into a large excess of ice-cold saturated sodium carbonate solution, the deep bluish-violet coloration first given changing to dark red. After standing a day, the purplish-red, microcrystalline precipitate was filtered off; it appeared to be identical in all respects with the direct sulphonation product of the anhydro-base.

(c) *Sulphonation.* Four grams of the benzoic ester chloride were added cautiously to an ice-cold mixture of 96 per cent. sulphuric acid (20 c.c.) and 20 per cent. oleum (4 c.c.). After standing one hour, a further 20 c.c. of 20 per cent. oleum was added, the temperature being allowed to rise to about 30°. The dark green solution was then poured at once into saturated brine, and the pale blue-green precipitate filtered off, washed with brine, then with glacial acetic acid, pressed, and dried. The product was similar in appearance to the acid sulphate of Anthranol Blue, but had quite different properties, as it dissolved in water to a deep blue solution which became purple on adding alkali, but the liquid remained clear, no precipitate being formed. The purple solution was quite stable at room temperature for several days and the alcoholic solution of the blue-green salt became purple on adding alkali without any formation of precipitate, hence the benzoyl group had not been split off. The bluish-green substance is therefore the acid sulphate of the sulphonic acid of the benzoic ester chloride of formula IX.

Experiments on the sulphonation of the toluene-*p*-sulphonyl derivative of Anthranol Blue gave similar colour reactions to those described under (c), but the investigation was not pursued further.

Summary

(1) Michler's ketone chloride condenses with anthrone to form a substance, $C_{21}H_{24}ON$, which appears to be 4':4''-tetramethyl-

diaminodiphenyl-9:10-anthraquinomethane or, shortly, 4':4''-tetramethyldiaminoanthrafuchsone, a bright brick-red, crystalline substance melting at 264°-265°.

(2) The above substance (called the anhydro-base) forms intensely blue salts of a dye, termed Anthranol Blue, which are derived from the hypothetical enolic form of the hydrated carbinol base; the salts are immediately hydrolysed by water to form an unstable violet-black imonium base, which loses water readily and is reconverted into the anhydro-base.

(3) Treatment with acylating agents such as benzoyl chloride or pyridine-acetyl chloride leads to the formation of the chloride of the acyl ester corresponding to the hypothetical enolic base. These substances are sparingly soluble in water, but are sufficiently stable to give fine blue shades on wool, silk, and mordanted cotton, which are not, however, fast to boiling.

(4) Fuming sulphuric acid acts upon the anhydro-base to give a very soluble product, which forms red salts, but is devoid of tinctorial properties; it is probably a tetramethyldiaminophenylbenzanthrone-sulphonic acid.

(5) Fuming sulphuric acid may act upon the benzoic ester chloride in two ways, either by hydrolysing the benzoyl group with or without subsequent sulphonation, or it may effect simple sulphonation of the benzoic ester to give a product forming a deep blue salt having the character of an acid dye, but which is turned violet by alkalis.

The author's thanks are due to Professor W. H. Perkin, F.R.S., for valuable suggestions and for the interest he has taken in the work, and to the British Dyestuffs Corporation, Ltd., for permission to publish the results. The very accurate analyses were carried out by Mr. F. Hall.

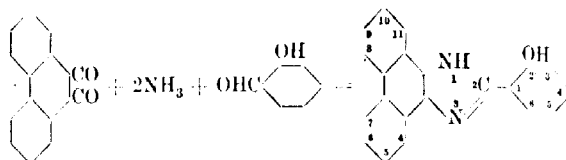
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[Received, April 15th, 1923.]

(LXXIV).--*Dyes Derived from Phenanthraquinone.* *Part III. Phenanthriminazoles.*

By ANUKUL CHANDRA SIRCAR and GOPAL CHANDRA SIRCAR.

JAPP and WILLOCK (T., 1880, 37, 661; 1881, 39, 225) and Japp and Streetfield (T., 1882, 41, 146) have shown that phenanthraquinone condenses with benzaldehyde in presence of ammonia to form an oxazole derivative, but with hydroxy-aldehydes under similar conditions, iminazoles are obtained.



The hydroxyphenylphenanthrimazoles are colourless. In view of the fact that heterocyclic rings containing two nitrogen atoms are generally chromophoric (for example, the eurihodies and safranines), it was thought that this property of the five-membered ring in phenylphenanthrimazole might be developed by substituting suitable groups in the phenanthrene and the benzene nuclei, and that the iminazoles thus obtained might possess tinctorial properties. Some dyes of the benziminazole series are already known (Leilmann and Hailer, *Ber.*, 1893, **26**, 2760).

With that object in view, the work of Japp and his collaborators (*loc. cit.*) has been extended, and it has been found that, like the hydroxy-aldehydes, aromatic nitro-aldehydes and bromohydroxy-aldehydes condense with phenanthraquinone and its substituted derivatives, in presence of ammonia, to form phenanthrimazoles.

Derivatives of 2-phenylphenanthrimazole have been prepared containing substituents in the following positions: 3'-nitro-; 7-; 8-; (1)-dibromo-3'-nitro-; 5-; 10-dibromo-3'-nitro-; 5-bromo-3'-nitro-; 3'-nitro-5-; 10-dianilino-; 3'-nitro-7-; 8-dianilino-; 3'-nitro-5-amino-; 3'-nitro-7-; 8-dihydroxy-; 3'-nitro-5-; 10-dihydroxy-; 7-; 8-; (1)-dibromo-4'-nitro-; 5-bromo-2'-hydroxy-; 5'-; 7-; 8-; (1)-tribromo-2'-hydroxy-; and 3'-; 5'-; 7-; 8-; (1)-tribromo-4'-hydroxy-.

The introduction of auxochrome groups in the benzene ring is not accompanied by a deepening of the colour. The iminazoles obtained from phenanthraquinone itself are either colourless or pale yellow, whilst those obtained from hydroxy- and amino-phenanthraquinones all have well-developed tinctorial properties.

The presence of anilino-groups has the effect of deepening the colour of some series of dyes (Sircar and Dutt, T., 1922, **121**, 1944; Eng. Pat. 9311 of 1915, etc.). It has now been found that anilino-groups can be easily introduced in the phenanthrimazole series by Ullmann's method (*Ber.*, 1901, **34**, 2174), the following anilino-2-phenylphenanthrimazoles having been prepared from the corresponding bromo-2-phenylphenanthrimazoles in that way: 3'-nitro-7-; 8-; (1)-dianilino-; 3'-nitro-5-; 10-dianilino-; 4'-nitro-7-; 8-; (1)-p-dianilino-; 5'-anilino-2'-hydroxy-; 5'-; 7-; 8-; (1)-tri-anilino-2'-hydroxy-; and 3'-; 5'-; 7-; 8-; (1)-tri-anilino-4'-hydroxy-.

The colour developed on the fibre by these anilino-phenylphen-

anthriminazoles' is markedly influenced by the position of the anilino-group. Situated in the benzene nucleus, it produces shades ranging up to violet only, but its introduction into the phenanthrene nucleus causes an appreciable deepening of the colour on the fibre; in this respect, the phenanthriminazoles resemble the phenanthranaphthazines (Sircar and Dutt, *loc. cit.*). The simultaneous introduction of anilino-groups into both nuclei produces better results, shades ranging even up to bluish-black being obtainable.

The phenanthriminazoles are stable substances of high melting point, and give characteristic colorations in concentrated sulphuric acid solution. They are remarkably insoluble in the ordinary solvents; most of them can, however, be crystallised from pyridine.

Although almost insoluble in water, the phenanthriminazoles when freshly precipitated from concentrated sulphuric acid solution are fairly well adapted for dyeing on wool: in several cases, it was found advantageous to use chrome-mordanted wool.

EXPERIMENTAL.

Japp's method (*loc. cit.*) for the preparation of phenanthriminazoles is not quite suitable when dealing with small quantities of material. The best result in those circumstances was obtained by the following method: The quinone and the aldehyde were dissolved in a minimum of hot amyl alcohol and a current of dry ammonia was rapidly passed through the well-stirred solution: the condensation product separated on cooling. In some cases, it was found advantageous to heat the mixture of the quinone, aldehyde, and strong ammonia under pressure at 140–180° for three to four hours.

These methods will be referred to in the sequel as the "alcohol method" and the "autoclave method," respectively.

3'-Nitro-2-phenylphenanthriminazole.—The yellow, crystalline flocks obtained by gradually cooling a solution of phenanthraquinone (2 grams) and *m*-nitrobenzaldehyde (2 grams) in 160 c.c. of boiling amyl alcohol after a current of dry ammonia had been passed for a few minutes, separated from pyridine in yellow needles melting at 240° with decomposition (Found: N = 12.61. $C_{21}H_{13}O_2N_3$ requires N = 12.38 per cent.).

7:8(?)-Dibromo-3'-nitro-2-phenylphenanthriminazole, prepared in the same way as the preceding compound from dibromophenanthraquinone (1.8 grams) [D.R.P. 222,06] and *m*-nitrobenzaldehyde (2 grams), crystallised from acetone in clusters of yellow, prismatic needles, not melting below 285°. It is sparingly soluble in acetic acid or alcohol, insoluble in chloroform, water, or benzene, and readily soluble in pyridine, aniline, or nitrobenzene. With

concentrated sulphuric acid, it gives a characteristic grass-green coloration (Found: Br = 32.07. $C_{22}H_{11}O_2N_3Br_2$ requires Br = 32.19 per cent.).

5 : 10-Dibromo-3'-nitro-2-phenylphenanthriminazole, prepared in the same way as the last compound from 2 : 7-dibromophenanthraquinone, separated from pyridine in yellow needles, not melting below 290°. It is insoluble in acetone, alcohol, chloroform, or water, and soluble in aniline or nitrobenzene. It gives a bottle-green coloration with sulphuric acid and dyes a yellowish-brown shade on wool (Found: Br = 31.78. $C_{22}H_{11}O_2N_3Br_2$ requires Br = 32.19 per cent.).

5-Bromo-3'-nitro-2-phenylphenanthriminazole, obtained from 2-bromophenanthraquinone (1.5 grams) and *m*-nitrobenzaldehyde (1.2 grams), crystallised from pyridine in yellow needles, melting at 280° with decomposition after shrinking at 270°. It is insoluble in all the common organic solvents, and gives a greenish-yellow coloration with sulphuric acid (Found: Br = 18.88. $C_{21}H_{12}O_2N_3Br$ requires Br = 19.14 per cent.).

3'-Nitro-5 : 10-dibromo-2-phenylphenanthriminazole. One gram of 2 : 7-diaminophenanthraquinone and 0.8 gram of *m*-nitrobenzaldehyde were dissolved in 200 c.c. of boiling amyl alcohol and the solution, after being cooled in a freezing mixture, was saturated with dry ammonia. Ten days later, the brown precipitate that had separated was crystallised from pyridine and obtained as a powder, not melting below 285°. It was insoluble in all the common organic solvents and gave a brownish-red coloration with sulphuric acid. It dyed mordanted wool in terra-cotta shades and chrome-mordanted wool in brown shades (Found: N = 18.27. $C_{21}H_{12}O_2N_3$ requires N = 18.67 per cent.).

The same compound was prepared by the autoclave method (1 gram of diaminoquinone, 1 gram of *m*-nitrobenzaldehyde, 20 c.c. of strong ammonia; temperature 180°). The black mass obtained after filtration was crystallised from pyridine (Found: N = 18.39 per cent.).

3'-Nitro-7 : 8-diamino-2-phenylphenanthriminazole, prepared from 4 : 5-diaminophenanthraquinone (1 gram), *m*-nitrobenzaldehyde (1 gram), and strong ammonia (20 c.c.) by the autoclave method (three and a half hours at 170°–180°), was obtained as a crystalline powder (from pyridine), not melting below 290°. All its properties are similar to those of the preceding compound (Found: N = 19.22 per cent.).

3'-Nitro-5-amino-2-phenylphenanthriminazole. The product obtained from 2-amino-phenanthraquinone (1 gram), *m*-nitrobenzaldehyde (0.9 gram), and 20 c.c. of strong ammonia (autoclave

method; 140–150° for four hours), separated from pyridine as a light brown, crystalline powder melting above 285°. It gave a blood-red coloration with sulphuric acid and dyed chrome-mordanted and unmordanted wool in brown shades (Found: C = 71.69; H = 3.85; N = 15.07. $C_{21}H_{14}O_2N_4$ requires C = 71.19; H = 3.95; N = 15.82 per cent.).

3'-Nitro-7:8-dihydroxy-2-phenylphenanthriminazole.—The product obtained from 4:5-dihydroxyphenanthraquinone, the aldehyde, and ammonia by the autoclave method (160° for four hours) was purified by dissolution in sodium hydroxide solution and precipitation with dilute hydrochloric acid. It was insoluble in almost all organic solvents and did not melt below 290°. Whilst not absorbed by unmordanted wool, it dyes chrome-mordanted wool in buff-coloured shades.

3'-Nitro-5:10-dihydroxy-2-phenylphenanthriminazole was prepared from the 2:7-dihydroxy-quinone in a similar way and resembles the preceding compound in its properties. It gives deep brown shades on chrome-mordanted wool.

7:8(2)-Dibromo-4'-nitro-2-phenylphenanthriminazole.—The precipitate obtained by the alcohol method (1.8 grams of dibromophenanthraquinone [D.R.-P. 222206], 2 grams of *p*-nitrobenzaldehyde, 160 c.c. of amyl alcohol) crystallised from pyridine in clusters of yellow needles melting at 252° (decomp.). It was slightly soluble in acetone, acetic acid, or alcohol, insoluble in chloroform, benzene, or water, and readily soluble in nitrobenzene, aniline, or pyridine. It dyes wool in yellow shades (Found: Br = 32.71. $C_{21}H_{11}O_2N_3Br_2$ requires Br = 32.19 per cent.).

5'-Bromo-2'-hydroxy-2-phenylphenanthriminazole.—The crystalline mass obtained by the alcohol method (2 grams of phenanthraquinone, 2.2 grams of 5-bromo-salicylaldehyde, 150 c.c. of amyl alcohol) separated from acetone in white needles melting at 267°. It was sparingly soluble in alcohol or acetic acid, insoluble in chloroform, benzene, or water, and gave a blue coloration with sulphuric acid (Found: Br = 20.29. $C_{21}H_{13}ON_2Br$ requires Br = 20.57 per cent.).

5':7:8(2)-Tribromo-2'-hydroxy-2-phenylphenanthriminazole, prepared in a similar way to the preceding compound from dibromophenanthraquinone [D.R.-P. 222206] (2 grams) and 5-bromo-salicylaldehyde, separated from pyridine in straw-white needles, not melting below 285°. It gave with sulphuric acid a bluish-green coloration (Found: Br = 43.71. $C_{21}H_{11}ON_2Br_3$ requires Br = 43.81 per cent.).

3':5':7:8(2)-Tetrabromo-4'-hydroxy-2-phenylphenanthriminazole, obtained from 3:5-dibromo-4-hydroxybenzaldehyde and the

dibromo-quinone of D.R.-P. 222206 in a similar way to the last compound, crystallised from pyridine in white needles, melting at 275° (decomp.) after shrinking at 267° . It dissolves in sulphuric acid with a green colour (Found: Br = 50.83. $C_{21}H_{10}ON_2Br_2$ requires Br = 51.12 per cent.).

3'-Nitro-7:8-dianilino-2-phenylphenanthriminazole.—The product obtained by boiling 1 gram of the corresponding dibromo-iminazole (*vide supra*) under reflux for two to three hours with 10 grams of aniline and 0.2–0.3 gram of copper powder (Ullmann, *loc cit.*) was filtered hot into dilute hydrochloric acid. The green precipitate was purified by washing, digestion with concentrated sulphuric acid, and precipitation with water; it was finally boiled with dilute hydrochloric acid. The substance is only slightly soluble in pyridine or aniline, and insoluble in other solvents. It does not melt at 283° , gives a characteristic green coloration with sulphuric acid, and dyes chrome-mordanted wool in brownish-green shades and unmordanted wool in grass-green shades (Found: N = 13.13. $C_{33}H_{25}O_2N_5$ requires N = 13.43 per cent.).

3'-Nitro-5:10-dianilino-2-phenylphenanthriminazole was prepared in the same way as the preceding compound from the 2:7-dibromo-iminazole described above. The dark green, flocculent mass obtained was dried, dissolved in boiling pyridine, precipitated by hot water, and finally boiled with dilute hydrochloric acid. Unlike the other anilino-iminazoles described in this paper, it does not melt below 290° . It gives an olive-green coloration with sulphuric acid and dyes wool in leaf-green shades and chrome-mordanted wool in olive-green shades (Found: N = 13.04. $C_{33}H_{25}O_2N_5$ requires N = 13.43 per cent.).

3'-Nitro-5-anilino-2-phenylphenanthriminazole was prepared from the 2-bromo-iminazole (*vide supra*) and purified in a similar way to the preceding compound. It was obtained as a bluish-green powder giving a dark-green coloration with sulphuric acid and dyeing chrome-mordanted or unmordanted wool in ash-coloured shades (Found: N = 12.6. $C_{27}H_{17}O_2N_4$ requires N = 13.33 per cent.).

4'-Nitro-7:8-dianilino-2-phenylphenanthriminazole, obtained by subjecting the corresponding dibromo-iminazole to Ullmann's reaction, was dissolved in cold concentrated sulphuric acid, precipitated with water, and finally boiled with dilute hydrochloric acid. It gives a reddish-green coloration with sulphuric acid and dyes wool in leather-brown shades and chrome-mordanted wool in yellowish-brown shades (Found: N = 12.8. $C_{33}H_{25}O_2N_5$ requires N = 13.43 per cent.).

5'-Anilino-2'-hydroxy-2-phenylphenanthriminazole, prepared from the corresponding iminazole, separates from pyridine in bluish-

violet needles. It dissolves in sulphuric acid with a dark green colour, changing to maroon, and dyes mordanted and unmordanted wool in maroon shades (Found: N = 9.96. $C_{27}H_{19}ON_3$ requires N = 10.47 per cent.).

5' : 7 : 8(?) - *Trianilino-2'-hydroxy-2-phenylphenanthriminazole*, prepared from the corresponding bromo-compound, gives a dark green coloration with sulphuric acid and dyes wool in chocolate shades and chrome-mordanted wool in maroon shades (Found: N = 11.88. $C_{39}H_{29}ON_5$ requires N = 12.00 per cent.).

3' : 5' : 7 : 8(?) - *Tetra-anilino-4'-hydroxy-2-phenylphenanthriminazole*, prepared in the usual way from the corresponding bromo-compound, dyes unmordanted wool in bluish-black shades and chrome-mordanted wool in bluish-green shades. It develops a bluish-green coloration in sulphuric acid.

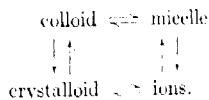
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[Received, March 12th, 1923.]

CLXXV.—*The Protective Action of Potassium Oleate on Gold Sols in Water-Alcohol Mixtures.*

By ERIC KEIGHTLEY RIDEAL and LOUIS LEIGHTON BIRCUMSHAW.

IREDALE (I., 1921, 119, 625), in investigating the protective action of soaps on gold solutions, showed that soaps, even in very dilute aqueous solutions, exerted a protective action on gold, whilst in alcohol no such protective action was to be observed. In consequence, it was argued that the hypothesis of McBain postulating a transition in the equilibrium



in favour of the crystalloidal state on progressive dilution could not be accepted. In addition, he pointed out that the protective action of the colloidal soap might be outweighed by the coagulating action of the kations, although part of the experimental data is not beyond criticism in that the dispersity of a gold solution prepared from auric chloride varies greatly with the p_H of the solution in which it is formed, and for the uniformity of which no precautions were taken.

Owing to the fact that the surface tension of water is lowered by the addition of very small quantities of soap, it follows from Gibbs's equation that the surface concentration exceeds that in

the bulk; consequently, the soap concentration at the gold-water interface may be sufficiently high to effect protection, although the circumambient solution is relatively dilute. Undoubtedly, as Iridale has shown, the protective action is not exerted by the soaps in the molecular state, but by both the neutral and acid soaps (shown to be present, especially in dilute solution, by McBain) either in the colloid or the micelle form.

Although an experimental method for determining the concentration of the soap at the gold liquid interface for various dilutions has not yet been elaborated, a comparison with the data derived from a study of surface tension measurements at the air-liquid interface should give an indication as to the magnitude of this change. It has recently been shown by one of us (this vol., p. 91), in a study of the density, viscosity, and surface tension of solutions of potassium oleate in water, in alcohol, and in mixtures of these, that dilution with alcohol is a convenient method for altering the relative concentrations of the various forms in which the soap can exist in solution, for the colloidal aggregate appears to break down in three distinct stages, extending over the ranges 0-15, 15-45, and 45-100 per cent. of alcohol by volume. It appears very probable that the colloidal aggregate has disappeared completely at a concentration of 50 per cent. of alcohol.

It was considered of interest to investigate the protective action of potassium oleate on gold solutions in alcohol-water mixtures and to determine how far an alteration in the dispersity occurred when the alcohol concentration was varied over the ranges indicated above.

EXPERIMENTAL

Materials. The potassium oleate was prepared in a similar manner to that used in the previous work (*loc. cit.*).

The gold chloride solution contained 6 grams per litre of the hydrated chloroauric acid in accordance with the directions of Zsigmondy (*Kolloidchemie*, p. 150).

The general method of procedure was as follows: To 12 c.c. of the soap solution dispersed in the alcohol-water mixture, 0.25 c.c. of the gold chloride solution and 0.3 c.c. of a 0.18*N*-solution of pure potassium carbonate were added. As a reducing agent, both phosphorus, dissolved in ether, and hydroxylamine were employed. For the former, 0.25 c.c. of a saturated solution of phosphorus in ether diluted twenty-five times, and for the latter 0.25 c.c. of a 1 per cent. aqueous solution was found to give uniform results. Reduction in all cases was carried out at room temperature. The full colour in the case of reduction with phosphorus was developed only after twenty-four hours, whilst hydroxylamine effected reduc-

tion much more rapidly. In all cases, twice distilled water and carefully steamed boiling tubes were employed.

Although the colour of the light transmitted through gold solutions varies, not only with the size, but also with the shape (Steubing, *Ann. Physique*, 1908, **26**, 329; Garnett, *Phil. Trans.*, 1904, [A], **203**, 385), yet in general the solutions transmitting red light consist of finer particles than blue sols (Lanyea, *Sitzungsber. Akad. Wiss. Wien*, 1909, **118**, 867) and, in consequence, the colour change for solutions prepared under identically the same conditions may be accepted as a criterion of their dispersity. In a preliminary investigation, the following results were obtained :

0.1 per cent. Potassium oleate.

% Alcohol by volume.	Colour.	Remarks.
0.0	Very pale red.	
10.0	Pink.	
20.0	Red.	Abrupt colour change.
30.0	Reddish-purple.	
40.0	" "	
50.0	" "	
60.0	Bluish-purple.	Precipitated in forty-eight hours.
70.0	" "	Precipitated in twenty-four hours.
80.0	" "	Precipitated rapidly.
90.0	" "	" "

Thus between 20 and 30 per cent. of alcohol by volume a rapid change in the dispersity of the gold solution occurs, whilst between 50 and 60 per cent. of alcohol the potassium oleate loses all its protective properties. In addition, a slight break in the regular series was to be noted within the range 0—10 per cent.

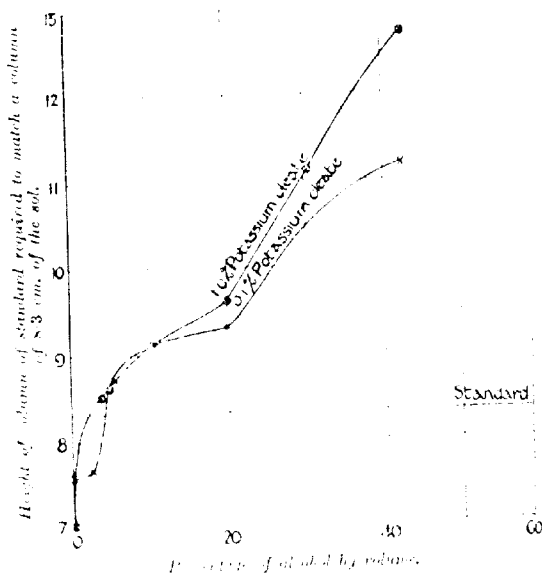
A more detailed examination of the range 0—10 per cent. of alcohol and 20—30 per cent. of alcohol revealed the fact that the colour became markedly more intense between 3 and 4 per cent. of alcohol by volume, which increase continued up to 10 per cent. of alcohol, after which the colour increase in solution became less marked until a relatively sharp break in the colour change, red to reddish-purple, took place within the concentration range 26—28 per cent. of alcohol.

The data on the surface tension of the solutions indicate that the surface tension* of the oleate solution and mixed solvent is identical at 50 per cent. of alcohol, confirming the fact that in mixed solvents, as it has been shown for single solvents, the surface tension depressant is the protective agent.

On dilution of the solutions prepared in this manner, it was found possible to make a somewhat approximate comparison between them by means of a simple tintometer. As standard, an unprotected red-gold solution was prepared according to Zsigmondy's

method, and the red colour of the solutions prepared with the alcohol-water mixtures was matched against this. As the solutions increased in grain size, the matching of the red colour, even in extreme dilutions, was found to be increasingly difficult; nevertheless, the dilutions at which breaks in the curve, obtained in this way, occurred were found to be approximately coincident with those obtained by the comparative visual method of colour change. The data obtained in this manner are indicated on the curve (Fig. 1).

FIG. 1.



With regard to the data obtained, it appears that the following changes in the dispersion of the solution can be detected.

- (1) A fairly rapid change commences on the addition of 2-3 per cent. of alcohol and this continues up to 10 per cent. of alcohol.
- (2) From 10-26 per cent., the change is relatively small.
- (3) From 26 per cent., the change is fairly rapid up to 50 per cent. of alcohol, when protective action vanishes.

The ordinary visual method and the method of matching agree with the exception of the point 25 (visual) and 26 (by matching).

Discussion.

The study of the surface tension data for alcohol-water mixtures, both with and without soap, indicated that on dilution to 50 per cent. of alcohol by volume the surface tension of the solution is unaltered by the addition of the soap. Evidently the surface tension depressant, either the micelle or colloidal soap, is entirely converted into a non-capillary active form in this medium. At the same dilution, such solutions have lost all their protective action on gold sols. Thus it appears probable that the concentration of soap at the gold-liquid interface does not differ much from that existing at the air-liquid surface, otherwise the effect of mass action on the equilibria of the various forms of soap on the two surfaces would necessitate a solvent of varying peptising power for each interface, that is, a different alcohol content; in addition, it appears that the protective action of soap is due to a surface concentration in the colloidal or micelle form.

The initial rapid change in the protective power within the range 0–10 per cent. of alcohol coincides with a rapid fall in the viscosity (*loc. cit.*) of such solutions and may possibly be due to the comparatively rapid peptisation or partial destruction of the coarser colloid particles on the addition of the first portions of alcohol to an aqueous solution of potassium oleate.

Neither by viscosity nor from surface tension data is any abrupt change to be noted within the range 15–45 per cent. of alcohol. The protective action, however, suffers but little change between the range 10 and 26 per cent., and thereafter the change is more rapid until protective action ceases. The addition of alcohol exerts a twofold effect: it both decreases the ionisation of the micelle and increases the peptising power of the solvent. Owing to the fact that the micelle form is charged, it is probably less stable than the colloid. Thus on the addition of alcohol to the solution we may anticipate the destruction of the micellar form to take place before that of the colloidal form. It is possible that the range 10–26 per cent. of alcohol represents the gradual removal of the micellar form, and the second portion the complete peptisation of the remaining colloidal soap.

Summary.

The protective action of potassium oleate on gold sols, prepared in alcohol-water mixtures, has been examined. The protective action is found to vary with the alcohol content, exhibiting three well-defined ranges, 0–10 per cent., 10–26 per cent., and 26–45 per cent. Above 50 per cent. of alcohol, the solution exerts no protective power. The protective action is compared with the

alteration of the viscosity and the surface tension of such solutions, and it is shown that the capillary active material, either the colloidal or micellar form, is the protective agent. Reasons are given for the hypothesis that the colloidal form is more protective than the micellar. The surface concentration of soap at the gold-liquid interface apparently runs parallel to the surface concentration at the liquid-air interface.

DEPARTMENT OF PHYSICAL CHEMISTRY,
CAMBRIDGE.

(Received, May 2nd, 1922.)

CLXXVI.—*The Isomerism of Reduced Derivatives of Quinoxaline. Part I. The Four Stereoisomeric 2:3-Diphenyl-1:2:3:4-tetrahydroquinoxalines.*

By GEORGE MACDONALD BENNETT and CHARLES STANLEY GIBSON.

THE reduction of 2:3-diphenylquinoxaline was shown by Hinsberg and König (*Ber.*, 1894, **27**, 2181) to produce two isomeric 1:2:3:4-tetrahydro-bases. On account of the presence of two similar asymmetric carbon atoms in the molecule $C_{16}H_{14} \begin{smallmatrix} \text{NH-CHPh} \\ \text{NH-CHPh} \end{smallmatrix}$ two optically active and two inactive isomerides should be capable of existence, the case being analogous to the classical one of the stereoisomeric tartaric acids.

The four bases theoretically possible have now been prepared. The "α-base" described by Hinsberg and König was resolved by means of the *d*- and *l*-camphor-*p*-sulphonic acids, and the optically active bases have been obtained in enantiomorphous, crystalline forms. The melting-point curve of one of the optically active bases with the inactive "α-base" indicated that the latter is a racemic compound and not a mixture. The "β-base" could not be resolved and therefore is the internally compensated isomeride. The isomeric bases are:

	M. p.	M_d^{20}
<i>l</i> -2:3-Diphenyltetrahydroquinoxaline (racemic)	135–135.5	156.2
<i>d</i> -2:3-Diphenyltetrahydroquinoxaline (racemic)	135–135.5	155.7
<i>racemic</i> 2:3-Diphenyltetrahydroquinoxaline (racemic)	106°	(The "α-base" of H. and K.)
<i>racemic</i> 2:3-Diphenyltetrahydroquinoxaline (internally compensated)	142–143°	(The "β-base" of H. and K.)

The diacetyl derivatives of the optically active bases are opposite in rotatory power to those of the corresponding bases. These have the following constants:

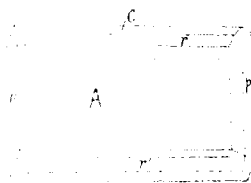
	M. p.	$M_{\text{calc.}}^{20}$
Diacetyl derivative of <i>l</i> -base	190-191°	164.3°
Diacetyl derivative of <i>d</i> -base	190-191°	165.3°

EXPERIMENTAL.

meso-2 : 3-Diphenyl-1 : 2 : 3 : 4-tetrahydroquinoxaline.

This, the most easily obtained of the isomeric bases, was prepared in the manner described by Hinsberg and König (*loc. cit.*). From alcohol, it crystallises in small, pale yellow needles, m. p. 142-143° (uncorr.) (Found : C = 83.6; H = 6.3. Calc., C = 83.9; H = 6.3 per cent.). Large crystals (Fig. 1) were obtained by the slow evaporation of an acetone solution.

Fig. 1.



Crystal system : Monoclinic; Class 5; Holosymmetric.

Habit : Tabular parallel to $A \equiv \{100\}$.

Axial angle = $119^\circ 7'$. *Axial ratios*, $a : b : c = 2.367 : 1 : 2.038$.

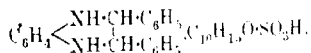
Forms observed, $A \equiv \{100\}$, $C \equiv \{001\}$, $p \equiv \{110\}$, $r \equiv \{011\}$.

Angle measured.	No. of measurements.	Limits.	Mean.	Calc.
$Ap \equiv (100) : (110)$	14	$63^\circ 37' - 64^\circ 37'$	$64^\circ 12'$	—
$Ar \equiv (100) : (011)$	13	$32^\circ 30' - 33^\circ 56'$	$32^\circ 57'$	—
$Cr \equiv (001) : (011)$	10	$27^\circ 34' - 28^\circ 58'$	$27^\circ 56'$	—
$pp' \equiv (110) : (110)$	12	$51^\circ 15' - 52^\circ 11'$	$51^\circ 33'$	$51^\circ 36'$
$Cr' \equiv (001) : (011)$	6	$51^\circ 40' - 53^\circ 25'$	$52^\circ 29'$	$52^\circ 20'$
$rp \equiv (011) : (110)$	10	$68^\circ 4' - 68^\circ 56'$	$68^\circ 32'$	$68^\circ 35'$
$Ar' \equiv (011) : (100)$	6	$66^\circ 26' - 66^\circ 46'$	$66^\circ 40'$	$66^\circ 47'$

The large face showed an extinction parallel to the b axis. The position of the optic axes could not be observed.

The diacetyl derivative of the base was prepared in the usual manner, and, as described by Hinsberg and König, was found to melt at $189-190^\circ$.

Salt with d-camphor-5-sulphonic acid.



was obtained crystalline by the careful addition of ether to a solution of equimolecular quantities of its components in ethyl acetate. It forms almost colourless plates belonging either to the monoclinic or to the triclinic system, the crystals being biaxial with one optic axis emerging approximately perpendicular to the large face. It melts with profound decomposition between 206°

and 213° (Found: C = 68.8; H = 6.6. $C_{30}H_{24}O_4N_2S$ requires C = 69.5; H = 6.57 per cent.). The salt showed no signs of resolution on repeated crystallisation. Its optical rotatory power, determined in pure ethyl alcohol ($c = 0.430$), was found to be $[\alpha]_{D_{589}}^{20} + 24.4^\circ$, whence $[M]_{D_{589}}^{20} + 126.5^\circ$. The base isolated from this salt was optically inactive.

Neither the β - nor the α -base of Hinsberg and König showed any signs of resolution into optically active components when condensed with *d*-hydroxymethylencamphor. A single crystalline compound was obtained in each case. This, therefore, constitutes a further case of the failure of this method of resolving externally compensated compounds (compare Gibson and Simonsen, *T.*, 1915, 107, 1148).

Resolution of Externally Compensated 2:3-Diphenyltetrahydro-quinoxaline into its Optically Active Components.

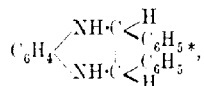
The externally compensated (or " α -") base (5.18 grams), obtained in the manner described by Hinsberg and König, was dissolved together with *d*-camphor- β -sulphonic acid (4.3 grams, 1 equivalent) in hot pure ethyl alcohol (60 c.c.). The crystals which separated during twenty-four hours consisted of the salt of the *l*-base in a practically pure condition. Further quantities of the same salt were obtained from the concentrated mother-liquor (3.85 grams in all). The base obtained from the final mother-liquor from this crystallisation by the addition of an aqueous solution of ammonia was dried and dissolved in pure ethyl alcohol together with an equivalent quantity of *l*-camphor- β -sulphonic acid, and yielded the salt of the *d*-base (1.7 grams, without working up the mother-liquor). These salts, after one recrystallisation from pure ethyl alcohol, showed equal and opposite rotatory powers in pure ethyl alcohol: *l*-B.L., $[\alpha]_{D_{589}}^{20} - 47.2^\circ$; *d*-B.L., $[\alpha]_{D_{589}}^{20} + 46.6^\circ$.

Instead of isolating the " α -base" in the somewhat laborious manner described by Hinsberg and König and then resolving it in the manner described above, the following method is to be preferred. 2:3-Diphenylquinoxaline (10 grams) is dissolved in hot ethyl alcohol (99.5–100 per cent.) (450 c.c.), and sodium metal (26 grams) added as rapidly as possible to the boiling solution. The solution is diluted with water containing acetic acid (70 c.c.) and the bases are removed with benzene. The benzene is removed in a current of steam, the mixed bases are separated, dried, and then dissolved in hot alcohol (420 c.c.). The crystals which separate from the solution on cooling consist chiefly of the main portion of the *meso*- or internally compensated base, and, after this

is removed by filtration, *d*-camphor- β -sulphonic acid (5 grams) is added to the filtrate, and the solution concentrated to 40 c.c. The salt, *lB dA*, which now separates, is filtered off and the base in the resultant mother-liquor separated in the usual manner by means of aqueous ammonia. This base after drying is treated in hot alcoholic solution with 1 equivalent of *l*-camphor- β -sulphonic acid and the *dB Li* salt crystallises out when the solution is allowed to cool.

1:2:3-Diphenyltetrahydroquinoxaline-d-camphor- β -sulphonate, $C_6H_4 \begin{smallmatrix} \diagup NH \cdot CH(C_6H_5) \\ \diagdown NH \cdot CH(C_6H_5) \end{smallmatrix} C_{10}H_{15}O_3SO_3H$, was crystallised once more from pure ethyl alcohol for final examination. It crystallises in small, doubly refracting, colourless needles, m. p. 245–252° (decomp.) (Found: C = 69.2; H = 6.5. $C_{30}H_{34}O_3N_2S$ requires C = 69.5; H = 6.57 per cent.). A determination of its optical rotatory power in pure ethyl alcohol ($c = 0.441$) gave $[\alpha]_{5461}^{20} = -56.9$, whence $[M]_{5461}^{20} = -294.5$.

1:2:3-Diphenyl-1:2:3:4-tetrahydroquinoxaline,



was liberated from the pure salt with *d*-camphor- β -sulphonic acid and recrystallised from ethyl alcohol. It melted at 135–135.5°. The melting point and optical rotatory power were both unchanged by further recrystallisation (Found: C = 83.6; H = 6.25. $C_{20}H_{18}N_2$ requires C = 83.9; H = 6.29 per cent.).

d:2:3-Diphenyl-1:2:3:4-tetrahydroquinoxaline was isolated in a similar manner from the salt with *l*-camphor- β -sulphonic acid. It melted at 135–135.5° (Found: C = 83.8; H = 6.0. $C_{20}H_{18}N_2$ requires C = 83.9; H = 6.29 per cent.).

The optical rotatory powers of these two bases were determined in pure ethyl alcohol at 20°:

l-base ($c = 0.733$): $[\alpha]_{5461}^{20} = -54.6^\circ$, -44.4° , -40.8° ; $[M]_{5461}^{20} = -156.2$.

d-base ($c = 0.416$): $[\alpha]_{5461}^{20} = +54.4^\circ$, $+43.8^\circ$, $+42.3^\circ$; $[M]_{5461}^{20} = +155.7$.

These two optical antipodes were found to crystallise in enantiomorphous forms (Figs. 2 and 3).

Crystal system: Monoclinic; Class 4: Sphenoidal.

Habit: Crystals obtained by slow evaporation of ethyl-alcoholic

* Thin and thick strokes are used to indicate the groups which are in the same plane.

solutions were tabular parallel to $p = \{110\}$. Others, formed in a cooling solution, had a sphenoidal habit with more complex faces. Crystals from acetone were tabular parallel to $B = \{010\}$.

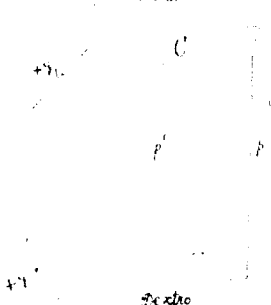
Axial angle $99^\circ 31'$. *Axial ratios*, $a : b : c = 0.6326 : 1 : 1.050$.

Forms observed. The simple combination of $C = \{001\}$, $B = \{010\}$, $p = +\{110\}$ and $p' = -\{110\}$ frequently occurred, simulating holosymmetry, the *l*- and *d*-crystals being indistinguishable. The enantiomorphism was shown by crystals having also

FIG. 2.



FIG. 3.



the forms $q = \{011\}$. Actually observed in the case of the *l*-base were: $q = \{011\}$, and sometimes $m = \{112\}$, $r = \{120\}$; in the case of the *d*-base, $q = \{011\}$ and, rarely, $s = \{023\}$.

Angle measured.	No. of measurements.	Limits.	Mean.	Calc.
Cp $\{001\} : \{110\}$	8	81.46° 82.8°	81.56°	
pB $\{110\} : \{010\}$	6	57.49° 58.13°	58.2°	
Cq $\{001\} : \{011\}$	5	45.34° 46.16°	46.0°	
pp' $\{110\} : \{110\}$	5	63.48° 64.12°	64.2°	63.56°
pB $\{011\} : \{010\}$	5	43.47° 44.12°	44.0°	44.0°
pB' $\{010\} : \{001\}$	3	89.51° 90.4°	89.56°	90.0°

The *diacetyl* derivatives of the above two active bases were prepared in the usual manner. Recrystallised from ethyl alcohol, they were obtained in rosettes of almost colourless needles. They both melted at $190-191^\circ$ and it is interesting to note that the optical rotatory power of the diacetyl derivative is opposite from that of the base from which it is prepared. Only the diacetyl derivative of the *l*-base was analysed (Found: C = 77.5; H = 6.3. $C_{21}H_{22}O_2N_2$ requires C = 77.8; H = 6.0 per cent.). The optical rotatory powers were determined in pure ethyl alcohol:

$$\begin{aligned} \text{L-Form, } [\alpha]_D^{20} &= 0.423; [\alpha]_{5461}^{20} = 44.4; [M]_{5461}^{20} = 1643. \\ \text{D-Form, } [\alpha]_D^{20} &= 0.341; [\alpha]_{5461}^{20} = 44.7; [M]_{5461}^{20} = 1653. \end{aligned}$$

racemic-2 : 3-*Diphenyltetrahydroquinoline*.—The preparation of this base by the slow evaporation of the alcoholic mother-liquor remaining after removing the *meso*-base, the method described by Hinsberg and König (*loc. cit.*), is very tedious and unsatisfactory on account of the tendency of this more soluble base to oxidise whilst impure. It was found more convenient to mix exactly equal weights of the active antipodes in pure ethyl alcohol and to evaporate the solution under diminished pressure at the ordinary temperature. In this manner the base was obtained in small, almost colourless plates, m. p. 106°. Unfortunately, many attempts to obtain crystals suitable for goniometrical and optical observation were unsuccessful.

The melting points of a series of mixtures of this *dl*-base with the *d*-base were determined and the temperature-composition curve showed a marked depression and a eutectic point at about 100° corresponding to a composition of 15–20 per cent. of the *d*-base with 80–85 per cent. of the *dl*-base. The *dl*- (formerly known as the "x-") base is therefore a racemic compound.

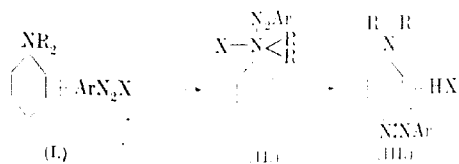
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[Received, May 7th, 1923.]

CLXXVII.—*Substitution in Vicinal Trisubstituted Benzene Derivatives. Part I.*

By WILLIAM DAVIES.

SOME of the most important views of the mechanism of aromatic substitution in vogue at the present day are well represented by those of Karrer (*Ber.*, 1915, **48**, 1398) and of Kurt Meyer. Karrer holds that where derivatives of phenols and amines are concerned, the reactant initially combines with the oxygen or nitrogen atom to form an ammonium or oxonium salt, which is then converted into the nuclear substitution product. For example, the action of an alkyldiazonium hydroxide or halide on a tertiary amine (I) is to form the intermediate compound (II), which then undergoes rearrangement with the loss of a molecule of water or halogen hydride to produce (III).



This principle is capable, with slight modifications, of wide application and harmonises, for example, with the ready rearrangement of phenylnitroamines into *o*- and *p*-nitroanilines, and of phenyl sulphate into the *o*- and *p*-phenolsulphonic acids. It explains, moreover, the remarkable ease with which amines and phenols cause substitution to take place, and throws light on the intermediate compounds isolated by Dimroth and Hartmann (*Ber.*, 1908, **41**, 4012) in the condensation of diazonium hydroxides with the enolic forms of desmotropic substances. The experimental evidence adduced by Karrer (*loc. cit.*) partly consists in showing that when the alkyl groups in (I) are large (for example, *isoamyl* radicles), the action of diazotised sulphanilic acid results in the formation of a mono-, and not the expected di-*isoamylaminoazo*-benzenesulphonic acid. Such a displacement usually occurs when the alkyl groups are large, and this fact receives its simplest explanation, in the terms of Karrer's theory, by assuming that one of these radicles is dislodged before the necessary intermediate compound of the type (II) can be formed. Similar anomalous couplings are known between phenyl ethers and diazonium derivatives. Moreover, the conception of addition to an oxygen atom preceding the formation of the final product has been used in other cases than aromatic substitution, as a basis of the mechanism of reaction. For example, Goldschmidt (*Z. Elektrochem.*, 1908, **14**, 581) explains esterification as taking place by means of the momentary quadrivalency of the oxygen atom of the alcohol.

The formation of azo-derivatives from diazonium compounds and certain hydrocarbons (Meyer and Schoeller, *Ber.*, 1919, **52**, 1468) shows that oxygen and nitrogen atoms are not peculiar in inducing coupling to take place, and that Kurt Meyer's theory of addition to a conjugated double bond system is the more probable explanation. Nevertheless, this coupling with hydrocarbons can be successfully carried out only under special conditions and with diazonium compounds containing acyclic substituents in the nucleus, and contrasts very forcibly with the ease of coupling with amines and phenols and their derivatives. It has consequently been thought worth while to investigate certain complicated problems in connection with the view of ascertaining whether the theory of Karrer can be modified to explain some anomalous cases.

Now when the substituent *b* in a compound of the type (IV) is in the ortho-position with regard to the two other substituents *a* and *c*, it is easy to imagine that steric influences may hinder the formation of any necessary intermediate compound by the agency of the substituent *b*. Not only may the well-known hindrance of

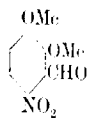
normal valency compounds occur in such cases, but instances are known of the similar prevention of the formation of molecular compounds. For example, Klages (*Ber.*, 1899, **32**, 1549) showed that 2:6-dimethylacetophenone was exceptional among the methyl and dimethyl derivatives of acetophenone examined in not forming a double compound with phosphoric acid. Moreover, Kenner and Parkin (*T.*, 1920, **117**, 852) have used a similar conception to explain the reactivity of some of the substituents already present in the benzene nucleus.



(IV.)



(V.)



(VI.)



(VII.)

The experimental portion of this communication centres round the nitration of *o*-veratraldehyde (V), which Perkin and Robinson (*T.*, 1914, **105**, 2389) showed is converted apparently entirely into (VI). This remarkable result might be explained by the above hypothesis of addition preceding substitution. The methoxy-group in the ortho-position to the aldehyde group would be sterically prevented from forming the intermediate compound (no matter whether the formation depends on the saturation of normal or partial valencies) and would consequently be expected to have no directing influence. The other methoxy-group, however, is not so obstructed, and would cause substitution to occur in the para-position with respect to it. As already pointed out, substitution actually does take place in this position. The result of nitrating *o*-vanillin (VII) does not contradict this view, because the hydroxyl group has a much smaller volume than the methoxyl group and a far greater directive influence.

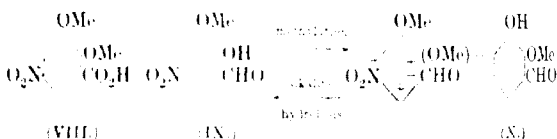
At the outset, it may be well to remark that the author is aware of instances that cannot be explained in this way at all. For example, the nitration of *o*-veratric acid (Cain and Simonsen, *T.*, 1914, **105**, 159) causes nitroxyl to enter the indicated position (VIII). This particular case, which is one of the very few exceptions to the rule of Robinson and Jones (*T.*, 1917, **111**, 906), made the necessity of this investigation more urgent.

In the course of the experiments now to be reviewed, where only one product has been obtained in bromination or nitration, the yield (which is given in the experimental part) shows that in almost all cases the reaction had gone to an extent of at least 75 per cent. in one direction. The remaining 25 per cent. is to be accounted

for by unavoidable loss in crystallisation and through working with comparatively small quantities.

The experimental work has first been concerned with finding the position of substitution in the bromination and nitration of *o*-vanillin. The bromo- and nitro-derivatives of *o*-vanillin have already been described by Rupp and Linek (*Arch. Pharm.*, 1915, **253**, 33), who assumed, without any supporting evidence, that the substituent enters the para-position with respect to the hydroxy-group. In view of the remarkable result of nitrating *o*-veratraldehyde ($V \rightarrow VI$), it seemed desirable to investigate the nitration and bromination of *o*-vanillin more thoroughly. This has been done and the assumption of Rupp and Linek confirmed.

The nitration product (IX) of *o*-vanillin is methylated and this nitro-veratraldehyde which is different from the one obtained by the nitration of *o*-veratraldehyde—is readily converted into the original nitro-*o*-vanillin by the action of alkali; no trace of an isomeric nitro-*o*-vanillin is obtained in the process. This retrograde step is excellent proof that the nitroxyl is in the meta-position to the aldehyde group, for if the nitroxyl were in any other position in the nucleus, the other methoxy-group would be loosened and alkaline hydrolysis (which would not very readily take place) would largely result in the formation of a nitro-derivative of *is o*-vanillin (X). This activating influence of meta-directing (especially sulphonyl and nitro-) groups on ortho- and para-substituent is often one of the simplest means by which the constitution of the aromatic substance in question can be decided.

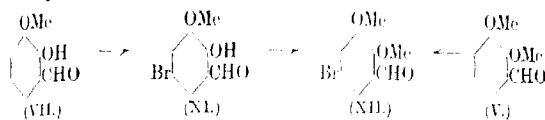


In this particular instance the formula for nitro-*o*-vanillin (IX) has been still further confirmed by its conversion into the corresponding 5-nitro-*o*-veratric acid (VIII), the constitution of which is definitely known (Chen and Simonsen, *loc. cit.*).

The bromo-derivative (XI) of *o*-vanillin, when methylated and nitrated, is easily converted into an indigotin derivative* by the action of acetone and sodium hydroxide solution. This fact shows

* Since the colour of indigotin is not greatly modified by methoxy-substituents, the author has not examined in detail the derivatives of indigotin prepared in the course of this investigation. All these derivatives closely resemble indigotin itself in appearance and in its sparing solubility in organic solvents.

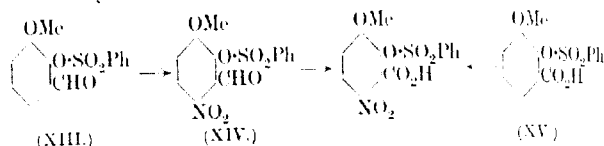
that the bromine atom cannot be in the ortho-position with respect to the aldehyde group, and therefore it is extremely probable that it is in the position indicated. This probability is still further enhanced by the fact that the methylation product (XII) of bromo-*o*-vanillin is identical with the bromination product of *o*-veratraldehyde.



In the bromination and nitration of *o*-veratraldehyde, the reversal of the positions taken up is apparently complete. This seems to be the best example yet known of the phenomenon of the occasional dependence of the position of substitution on the nature of the entering group. Other striking instances of this sort of phenomenon (apart from substitutions with mercury, which are only superficially abnormal) are the bromination and nitration of 4-nitro-veratrole investigated by Jones and Robinson (T., 1917, **111**, 905), the chlorination and nitration of 2-chloro-*p*-toluenesulphonyl chloride (Davies, T., 1921, **119**, 859) and of 2-chloro-*p*-nitrotoluene (*idem*, T., 1922, **121**, 806), and the bromination and nitration of 2-methoxy-3-ethoxybenzaldehyde described below, although the last have not yet been completely investigated. The author is at present unable to advance any consistent interpretation of the above remarkable reactions, and it is difficult to devise an explanation that agrees with the constancy of substitution in the vast majority of simple cases. Possibly the difference in molecular volume and molecular density of the entering groups is an important factor in deciding the position taken up, especially in polysubstituted benzene derivatives, where the effect of the entering group is chiefly noticeable. It must, however, be mentioned that, in the anomalous instances mentioned above the tendency pointed out by Robinson (*Annual Reports*, 1921, 83) "for the entrance of halogen to be definitely directed by positive groups to the meta-position to a greater extent than is the case when the entering substituent is nitroxy," is observed throughout.

In view of the remarkable contrast in the position of substitution shown in the nitration of *o*-veratraldehyde and *o*-veratric acid, it is of interest to ascertain whether, by suitable modification of the middle group in both aldehyde and the corresponding acid, similar substitution can be induced to take place in each case. The acetyl derivative of *o*-vanillin has accordingly been nitrated, but complete hydrolysis of the acetyl group apparently occurs during the process.

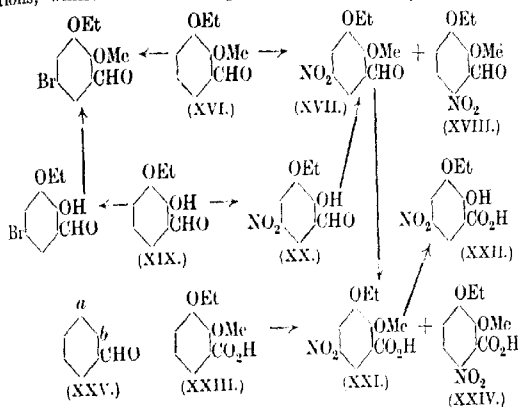
2-Benzenesulphoxy-3-methoxybenzaldehyde (XIII) is, however, nitrated much more smoothly and the product isolated (though the yield is only about 50 per cent.) is 6-nitro-2-benzenesulphoxy-3-methoxybenzaldehyde (XIV), which can be converted into a derivative of indigotin. It is, moreover, transformed by oxidation into an acid identical with the nitration product of 2-benzenesulphoxy-3-methoxybenzoic acid (XV).



It is thus clear that when the para-directive power of the hydroxyl group in *o*-vanillin and the corresponding acid is sufficiently weakened by connexion with suitable groups, the methoxy group will, in both instances, cause substitution to take place in the position para to itself. The nitration of *o*-vanillin derivatives is thus brought into line with that of derivatives of vanillic acid (compare Klemenc, *Sitzungsber. K. Akad. Wiss. Wien*, 1913, 422, 1343) and of guaiacol (Cardwell and Robinson, *T.*, 1915, 407, 255). Hence nitro-derivatives of *o*-vanillin and the corresponding acid, containing the nitro-group in the meta- or para-position with respect to the methoxy-group, can be prepared at will.

It has already been shown that in (XXV), when *a* is methoxyl and *b* hydroxyl, the two substitutions are entirely different (as far as nitration is concerned), and therefore moderate changes in the directing power of *a* and *b* cause complete change in the position of substitution. Hence it is of importance to consider the effect of extremely slight changes in the directive forces of *a* and *b*. 2-Methoxy-3-thoxybenzaldehyde (XVI) has accordingly been chosen for this purpose, as there is probably little difference in directing power between the two similar groups. The analogy with *o*-vanillin-aldehyde would indicate (XVIII) as the chief product, and this is the product that will be formed if the original idea of the effect of steric hindrance on substitution is valid. Experiment shows, however, that both (XVII) and (XVIII) are formed and that very probably (XVII) is the chief product. It can be isolated in nearly 50 per cent. yield from the nitration product, the presence of the other isomeride (XVIII) being shown by its conversion into a derivative of indigotin when treated with acetone and sodium hydroxide solution. It is hoped that the proportion of isomerides will be accurately determined by the action of ultra-violet light on a solution of the nitration product. 5-Nitro-2-methoxy-

3-ethoxybenzaldehyde (XVII) is entirely unaffected under these conditions, whilst the nitration product itself gives a greenish-blue



solution owing to the formation of a derivative of *o*-nitrosobenzoic acid (compare the action of ultra-violet light on *o*-nitrobenzaldehyde, Weigert and Kummerer, *Ber.*, 1913, 46, 1207). The elaboration of such a method of analysis is particularly desirable, in view of the difficulty encountered in the estimation of *o*-nitrobenzaldehyde in the nitration product of benzaldehyde (Brady and Harris, this vol., p. 489).

3-Ethoxysalicylaldehyde (XIX) is converted by nitration into 5-nitro-2-hydroxy-3-ethoxybenzaldehyde (XX), a reaction completely analogous to the nitration of *o*-vanillin. The methylated product is demethylated by boiling with dilute sodium hydroxide solution, the original nitroethoxysalicylaldehyde being regenerated. Moreover the acid (XXI) formed by oxidising the 5-nitro-2-methoxy-3-ethoxybenzaldehyde is converted by alkaline hydrolysis into a nitrohydroxyethoxybenzoic acid (XXII), and not a nitrohydroxy-methoxybenzoic acid. These observations, in the light of the remarks made on p. 1578, constitute a rigid proof of the accuracy of the formulæ in question.

The bromination of 3-ethoxysalicylaldehyde and 2-methoxy-3-ethoxybenzaldehyde leads, as in the bromination of *o*-vanillin and *o*-veratraldehyde, to derivatives in which the bromine atom is in the same position relative to the aldehyde group. It is noteworthy, however, that in the bromination of 2-methoxy-3-ethoxybenzaldehyde the yield of bromo-derivative is not so large as in the bromination of *o*-veratraldehyde. The bromine atom is not

adjacent to the aldehyde group, for the nitro-derivative of the bromination product of 2-methoxy-3-ethoxybenzaldehyde is readily converted into an indigotin derivative in the usual way. It is hence extremely probable that the formulæ of these bromine derivatives are correct, and that the bromination of 3-ethoxy-salicylaldehyde and its methyl derivative is perfectly analogous to the bromination of *o*-vanillin and *o*-veratraldehyde.

The nitration of 2-methoxy-3-ethoxybenzoic acid (XXIII) furnishes extremely interesting results when compared with the nitration of *o*-veratric acid. A mixture of two acids is formed, the one occurring in greater amount being 5-nitro-2-methoxy-3-ethoxybenzoic acid (XXI), m. p. 177°. There is also formed, however, another isomeric acid melting at 157.5°, to which the formula of 6-nitro-2-methoxy-3-ethoxybenzoic acid (XXIV) has tentatively been assigned. The correctness of this formula is fairly well established by the fact that when the nitration product (which contains XVII and a substance forming an indigotin derivative) of 2-methoxy-3-ethoxybenzoic acid is oxidised, only two acids are formed, one of which is the above 5-nitro-2-methoxy-3-ethoxybenzoic acid melting at 177°, and the other an acid which seems to be identical with the one melting at 157.5°. Completely conclusive evidence of the constitution of the acid melting at 157.5° will shortly be advanced.

Since the proportion of the isomerides formed in the nitration of 2-methoxy-3-ethoxybenzaldehyde has not yet been determined, the discussion of the bearing of the nitration of this substance and of the corresponding acid on the general question will be postponed. But even at this stage it is not premature to record that whilst it is still difficult to reconcile the results of the nitration of *o*-veratraldehyde and *o*-veratric acid, the original idea of the influence of steric hindrance on the position of substitution cannot in this sense be used as a generalisation. The research is, however, being continued, in order to obtain more information concerning the irregularities that occur in the orientation of vicinal trisubstituted benzene derivatives.

The description of the properties of the new substances prepared is to be found in the experimental portion of the paper. Attention, however, is here directed to the pungent and sternutatory properties of 2-methoxy-3-ethoxybenzaldehyde (XVI), which are considerably more pronounced than those of *o*-veratraldehyde. It should also be mentioned that no appreciable replacement of the aldehyde group by nitroxyl (compare Salway, T., 1909, 95, 1153) has been observed in the nitration of the ethers of these vicinal hydroxy-aldehydes.

EXPERIMENTAL.

Nitration and Bromination of o-Vanillin and its Derivatives.

*Preparation of 5-Nitro-2-hydroxy-3-methoxybenzaldehyde (IX).—**o*-Vanillin has already been nitrated by Rupp and Linck (*loc. cit.*), but as it is advisable for purposes of reference and comparison to give details of the method of nitration in acetic acid, the conditions used throughout the preparation are here described in full. A solution of nitric acid (5 c.c.; d 1.42) in acetic acid (20 c.c.) is slowly added with stirring and cooling to a cold solution of *o*-vanillin (15.2 grams) in 70 c.c. of glacial acetic acid. The reaction liquid becomes red, the temperature is maintained at 10–20°, and a pale yellow solid rapidly separates. This precipitate is collected after remaining over-night and when dry weighs 13.2 grams and melts at 140°. A further 2 grams can be obtained by diluting the acetic acid solution with water. 5-Nitro-2-hydroxy-3-methoxybenzaldehyde crystallises in very faintly yellow needles melting at 140–141°, whereas Rupp and Linck record 142° (Found: $N = 7.0$. Calc., $N = 7.1$ per cent.). It dissolves readily in most organic solvents and is slightly soluble in boiling water. The aqueous solution resembles that of picric acid, inasmuch as it is very much more yellow than the alcoholic or benzene solution. The sodium salt is slightly soluble in cold water, from which it separates in bright yellow needles.

5-Nitro-2:3-dimethoxybenzaldehyde.—The above described nitro-*o*-vanillin is not conveniently methylated by means of methyl sulphate, but the methylation is easily carried out by the application of Purdie's method. Nitro-*o*-vanillin (7.4 grams), dissolved in a mixture of methyl iodide (5 c.c.) and chloroform (30 c.c.), is boiled with finely powdered silver oxide (7 grams) for three hours. The inorganic matter is filtered off, and most of the solvent removed, when the methylated product (m. p. 115°) separates out in almost quantitative yield. Recrystallisation does not alter the melting point. 5-Nitro-2:3-dimethoxybenzaldehyde consists of colourless needles which are very soluble in hot and somewhat soluble in cold methyl alcohol, very slightly soluble in boiling water, and insoluble in cold sodium hydroxide solution (Found: $N = 6.4$. $C_8H_8O_5N$ requires $N = 6.6$ per cent.).

This nitro-*o*-veratraldehyde (0.2 gram) can be partly demethylated by boiling for a quarter of an hour with *N*-sodium hydroxide solution (20 c.c.). The clear orange-red solution, which becomes yellow on cooling, is filtered from unchanged nitro-*o*-veratraldehyde and acidified with hydrochloric acid. The light yellow substance produced melts at 138–141°, and after one crystallisation from

benzene, at 141°, alone or when mixed with a specimen of the original nitro-*o*-vanillin. This retrograde step is strong evidence in favour of the position assigned to the nitro-group in 5-nitro-2:3-dimethoxybenzaldehyde.

The accepted formula for this substance is confirmed by converting it by oxidation with potassium permanganate solution into the corresponding acid melting at 176° (uncorr.), which is the melting point of 5-nitro-*o*-veratric acid (Cain and Simonsen, *loc. cit.*). The acid is esterified by means of ethyl alcoholic hydrogen chloride, when the ethyl ester is obtained in colourless needles melting at 79°. The melting point is not depressed when this ester is mixed with an authentic specimen of ethyl 5-nitro-*o*-veratrate melting at 79°.

In order to render the nitration of *o*-veratraldehyde completely comparable with the nitration of *o*-vanillin and the bromination of *o*-veratraldehyde (see p. 1586), the nitration has been carried out in glacial acetic acid with the theoretical quantity of nitric acid. No rise of temperature or other sign of reaction is noticed when the reactants are mixed in the cold, but when the mixture is gently warmed on the water-bath for a quarter of an hour a definite reaction takes place. The product is kept over-night in a desiccator, when needles separate which melt at 88° and are identical in all respects with the nitroveratraldehyde obtained by Perkin and Robinson (*loc. cit.*).

To ascertain whether the remarkable contrast in the position of substitution which obtains in the nitration of *o*-veratraldehyde and of *o*-veratric acid holds for other derivatives of *o*-vanillin and their corresponding acids, certain derivatives of *o*-vanillin have been made and their nitration has been attempted, with the object of comparing the oxidised product with the substance produced by the nitration of the corresponding acid. Acetyl-*o*-vanillin (m. p. 76°), prepared by the ingenious method described by Rupp and Beyer (*loc. cit.*, p. 380), unfortunately cannot be nitrated by nitric acid in the cold. Even with the purest nitric acid, steady hydrolysis of the acetyl group takes place and the *o*-vanillin formed is then oxidised. By throwing the nitration product into water at different stages of the reaction, the only substance that can be isolated is unchanged acetyl-*o*-vanillin. Accordingly, the point at issue has been investigated with reference to 2-benzenesulphoxy-3-methoxybenzaldehyde (XIII).

2-Benzenesulphoxy-3-methoxybenzaldehyde, melting at 121°, prepared as described by Rupp and Linek (*loc. cit.*), is not smoothly nitrated owing to complicated reactions that occur when the solution in nitric acid is allowed to stand. Fairly good results

are obtained as follows: Benzenesulphoxymethoxybenzaldehyde (1 gram) is powdered and added at once to 20 c.c. of fuming nitric acid (d 1.5) at 12° . The temperature rises to 20° and a clear solution is formed, which after standing for ten minutes is poured into water. The product when dry melts at 120 – 135° , and after crystallisation from alcohol 0.6 gram of needles melting at 145° is obtained. A small amount of unchanged substance is also formed. 6-Nitro-2-benzenesulphoxy-3-methoxybenzaldehyde (XIV) consists of very faintly yellow needles which melt at 145° and become superficially greenish-blue on exposure to sunlight at the ordinary temperature (Found: $N = 4.3$. $C_{14}H_{11}O_7NS$ requires $N = 4.15$ per cent.). A solution of this substance (0.05 gram) in acetone (2 c.c.) is treated with a drop of concentrated sodium hydroxide solution and gently warmed and shaken until the solution becomes deep brown; it is at once diluted with about twice its volume of water and the solution boiled, when a derivative of indigotin rapidly separates in a very finely crystalline state. This method of preparing indigotins from *o*-nitrobenzaldehydes is very rapid and satisfactory.

6-Nitro-2-benzenesulphoxy-3-methoxybenzoic acid (XV) is prepared by the oxidation of the above aldehyde by means of potassium permanganate in the way indicated on p. 1587. The acid is obtained in excellent yield in colourless, glistening laminae melting at 218° , and can be conveniently recrystallised from dilute alcohol.

Nitration of 2-Benzenesulphoxy-3-methoxybenzoic Acid.—This acid is prepared in 80 per cent. yield by the oxidation of the corresponding aldehyde in the way described by Rupp and Linck (*loc. cit.*). The melting point (195°) of their acid is somewhat low, for it separates from alcohol in which it is only slightly soluble—in short, glistening crystals melting at 209° . The nitration of this acid takes place smoothly when one gram is dissolved in nitric acid (20 c.c.; d 1.5) at 10° and the solution kept over-night. When crystallised from alcohol, colourless plates (0.8 gram) melting at 218° are obtained. This substance is far more soluble in alcohol than the acid from which it is derived and a mixture of the two acids melts below 180° . On the other hand, when this nitro-acid (Found: $C = 47.7$; $H = 3.3$. $C_{14}H_{11}O_8NS$ requires $C = 47.6$; $H = 3.1$ per cent.) is mixed with that formed by the oxidation of 6-nitro-2-benzenesulphoxy-3-methoxybenzaldehyde, the melting point of the mixture is the same as that of its constituents.

It is clear from these experiments that whilst *o*-veratraldehyde and *o*-veratric acid cause nitration to take place in entirely different positions, 2-benzenesulphoxy-3-methoxybenzaldehyde and the corresponding acid orientate in the same place, as far as the introduction of nitroxyl is concerned.

Bromination of o-Vanillin.

5-Bromo-2-hydroxy-3-methoxybenzaldehyde (XI) is prepared exactly as described by Rupp and Linck by bromination in cold glacial acetic acid, when a yield of more than 80 per cent. of light yellow needles is obtained. No other substance can be isolated from the reaction product.

Methylation of Bromo-o-vanillin.—This reaction takes place much more smoothly by means of methyl sulphate than by Purdie's method. Bromo-*o*-vanillin (2 grams), dissolved in methyl alcohol (30 c.c.), is treated with 1.5 c.c. of methyl sulphate and an equivalent quantity of sodium hydroxide solution and boiled for half an hour. Methyl sulphate and sodium hydroxide solution are alternately added in very small quantities to the boiling solution until the slightest excess of either causes a change in colour. The time required is less than an hour and the volume of methyl sulphate used is 1.7 c.c. On cooling, the bromodimethoxybenzaldehyde (XII) separates out in almost quantitative yield in colourless, sterretatory needles melting at 81° (Found: Br = 32.3. $C_8H_8O_3Br$ requires Br = 32.6 per cent.). This methylation can also be successfully carried out without the aid of any organic solvent.

Bromination of o-Veratraldehyde. *o*-Veratraldehyde (3 grams), dissolved in 20 c.c. of glacial acetic acid, is treated in the cold with a solution of bromine (3.0 grams) in 4 c.c. of glacial acetic acid, whereby heat is evolved. The temperature is maintained at 10–20° for two days and the clear solution then poured into water, the solid precipitate washed, and dried in a vacuum. It weighs 3.7 grams and melts at about 70°. When recrystallised from methyl alcohol, the bromo-*o*-veratraldehyde separates in colourless needles melting at 81°, and weighs 3.1 grams. This substance is identical in all respects with the methylation product of bromo-*o*-vanillin, and the mixed substances melt sharply at 81°.

5-Bromo-6-nitro-2:3-dimethoxybenzaldehyde. One part of 5-bromo-2:3-dimethoxybenzaldehyde (this specimen was made by the methylation of bromo-*o*-vanillin) is dissolved in 20 parts of nitric acid (*d* 1.42) at 10–20°, and on standing the nitrated substance separates in a crystalline state, and is obtained in excellent yield by pouring the reaction product into water. This nitro-derivative is considerably less soluble in organic solvents than the original bromoveratraldehyde, and crystallises from methyl alcohol or glacial acetic acid in glistening, faintly yellow needles melting at 141° (Found: N = 4.9. $C_9H_8O_5NBr$ requires N = 4.8 per cent.). It is readily converted into a derivative of indigotin by the action of acetone and sodium hydroxide solution. Hence the bromine

atom is not in the ortho-position with respect to the aldehyde group.

5-Bromo-*o*-veratric Acid.—Half a gram of a specimen of 5-bromo-*o*-veratraldehyde (made by methylating *o*-vanillin) is suspended in a solution of magnesium sulphate (2 grams) in water (50 c.c.), and the boiling suspension gradually treated with a solution of potassium permanganate (0.4 gram) in 20 c.c. of hot water. When the permanganate solution is decolorised, the reaction product is cooled, shaken with 2*N*-sodium hydroxide solution (20 c.c.), and filtered cold, by which means any unchanged aldehyde is retained in the inorganic precipitate. The filtrate is acidified with hydrochloric acid and rapidly deposits clusters of colourless needles (0.4 gram) melting at 120° (Found: C = 41.5; H = 3.5; equivalent = 261. $C_9H_9O_4Br$ requires C = 41.4; H = 3.4 per cent.; equivalent = 258). This acid is slightly soluble in boiling and sparingly soluble in cold water. It was hoped that by distillation in a vacuum the acid would lose carbon dioxide and be transformed into a bromoguaiacol methyl ether, but unfortunately the acid is very stable and distills at a high temperature practically unchanged. The conversion of the nitro-derivative of *o*-veratric acid into this or an isomeric bromoveratric acid is also unexpectedly difficult to carry out, owing to the instability of the intermediate amino-*o*-veratric acid. It is hoped to submit, in a further communication, completely conclusive evidence of the position taken up by bromine in the bromination of *o*-vanillin.

Nitration and Bromination of 3-Ethoxysalicylaldehyde and its Derivatives.

3-Ethoxysalicylaldehyde (XIX), prepared by the firm of Haarmann and Reimer, Holzminden, does not seem to be described in the literature. The commercial product melts at 54–59°, but when purified by distillation in a current of steam it is obtained in long, light yellow needles melting at 64–65° and boiling with very slight decomposition at 263–264°/740 mm. (Found: C = 64.9; H = 6.1. Calc., C = 65.1; H = 6.0 per cent.). It possesses an extremely fragrant odour, much more pleasant than that of *o*-vanillin, and is readily soluble in organic solvents, but slightly soluble in water, the aqueous solution being distinctly yellow. The substance behaves like many other derivatives of salicylaldehyde; for example, it is volatile in steam, its alcoholic solution produces an indigo-blue coloration with ferric chloride solution, and it is easily converted into a scarlet *p*-nitrophenylhydrazone.

5-Nitro-2-hydroxy-3-ethoxybenzaldehyde (XX).—3-Ethoxysalicylaldehyde is nitrated in acetic acid solution with a slight excess of

nitric acid under the conditions described in the nitration of *o*-vanillin. 3-Ethoxysalicylaldehyde is less soluble in acetic acid than *o*-vanillin, and therefore 9 grams are dissolved in a comparatively large proportion (75 c.c.) of acetic acid, from which 6 grams of the nitration product crystallise on standing. It is perfectly pure, melts at 158° , and a further 2 grams can be isolated by diluting the filtrate with water and crystallising the precipitate from alcohol. This substance consists of small, light yellow crystals closely resembling the nitration product of *o*-vanillin (Found: N = 6.7. $C_9H_9O_5N$ requires N = 6.6 per cent.).

5-Nitro-2-methoxy-3-ethoxybenzaldehyde (XVII).—The above nitroethoxysalicylaldehyde is methylated by boiling with silver oxide and methyl iodide in chloroform, the reaction being complete in one hour. The yield is almost quantitative and the methylation product separates in very light, colourless needles melting at 118.5° (Found: C = 53.4; H = 4.9. $C_{10}H_{11}O_6N$ requires C = 53.3; H = 4.9 per cent.). No trace of an indigotin derivative is obtained by the action of acetone and sodium hydroxide solution on this nitrobenzaldehyde derivative. In order to examine the effect of sodium hydroxide solution the substance (0.1 gram) is boiled for five minutes with 2*N*-sodium hydroxide solution (8 c.c.), when a deep yellow solution is rapidly formed. The liquid, after being cooled, diluted, and filtered from unchanged substance, is acidified, when a light yellow substance at once separates. On crystallisation from ethyl alcohol, the precipitate is obtained in very light yellow crystals melting at 158° , and at this temperature when mixed with the original nitroethoxysalicylaldehyde. Hence demethylation and not de-ethylation is the main result of boiling this nitro-methoxyethoxybenzaldehyde with sodium hydroxide solution. This fact is very strong evidence in favour of the formula adopted, and the evidence is still further strengthened by the behaviour of the corresponding acid.

5-Nitro-2-methoxy-3-ethoxybenzoic Acid (XXI).—The above described nitromethoxyethoxybenzaldehyde (1.1 grams) is oxidised with a slight excess of potassium permanganate solution in the presence of magnesium sulphate exactly as described in the preparation of bromo-*o*-veratric acid (p. 1587). A small amount of the aldehyde remains unchanged and 0.8 gram of an acid melting at 177° is produced. This acid is very sparingly soluble in cold water, so much so that when a cold, fairly dilute aqueous solution of one of its salts is acidified, the acid is precipitated so rapidly as to appear amorphous to the naked eye. It can be crystallised from hot water, in which it is moderately soluble, or better from 90 per cent. ethyl alcohol, when it is obtained in colourless needles melting

at 177° (Found: equivalent = 241. $C_{10}H_{11}O_6N$ requires equivalent = 241). This acid gives no coloration with aqueous alcoholic ferric chloride solution.

5-Nitro-2-hydroxy-3-ethoxybenzoic Acid (XXII).—5-Nitro-2-methoxy-3-ethoxybenzoic acid (0.5 gram) is boiled with 2N-sodium hydroxide solution (75 c.c.), when a deep orange coloration is rapidly produced. After ten hours,* the solution is cooled, filtered from a trace of flocculent matter, and acidified with hydrochloric acid, when an acid (0.3 gram) melting at 205° is formed. 5-Nitro-2-hydroxy-3-ethoxybenzoic acid consists of colourless needles possessing a metallic sheen and sparingly soluble in cold water. Attempted purification does not alter the melting point of the acid first precipitated. The acid when treated with aqueous alcoholic ferric chloride solution gives an intense brownish-violet coloration which rapidly becomes brown. The analysis shows that the methoxy- and not the ethoxy-group has been hydrolysed (Found: C = 47.9; H = 4.1; equivalent = 226. $C_9H_8O_6N$ requires C = 47.6; H = 3.9 per cent; equivalent = 227). The equivalent is determined by direct titration of the acid with sodium hydroxide solution until a permanent orange-red solution is formed. This coloration is due to a trace of the disodium salt, and such a solution deposits large quantities of sodium 5-nitro-2-hydroxy-3-ethoxybenzoate in clusters of colourless needles very sparingly soluble in cold water.

Preparation of 2-Methoxy-3-ethoxybenzaldehyde.—3-Ethoxysalicylaldehyde (16.6 grams) is dissolved in methyl alcohol (80 c.c.) and a part of a solution of sodium hydroxide (5 grams of NaOH in 15 c.c. of water) added until the yellow sodium salt separates from the boiling methyl alcoholic solution. Methyl sulphate (10 grams) is at once added and the mixture boiled until the yellow colour disappears. The remaining sodium hydroxide solution is now added and also further 6 grams of methyl sulphate; after the reaction has gone on for a short time, the colour of the product can be changed from yellow to a singular green and from this back to yellow by alternate treatment with minute quantities of methyl sulphate and of sodium hydroxide solution, respectively. The reaction is now complete, the time required being about half an hour. The yellow solution is allowed to cool and diluted with water, when the desired methylation product separates as thick, colourless crystals (m. p. 45°) in a yield of 13 grams.

2-Methoxy-3-ethoxysalicylaldehyde can be recrystallised from

* The change in colour probably shows that the reaction is almost complete in a few minutes, but the reaction was allowed to proceed for ten hours to avoid any possibility of the presence of unchanged acid.

methyl alcohol and is slightly soluble in water, from which it separates in colourless needles melting at 45° . It is volatile in steam, has a burning taste, and when hot is extremely pungent and sternutatory, but is much less objectionable when cold (Found : C = 66.4; H = 6.55. $C_{10}H_{12}O_3$ requires C = 66.7; H = 6.7 per cent.).

Nitration of 2-Methoxy-3-ethoxysalicylaldehyde.—At least two isomerides are produced in this experiment. When the nitration is carried out with excess of nitric acid (d 1.42) at the ordinary temperature in the usual way and the nitration liquid diluted with water, the substance obtained melts at about 85° and produces a small amount of an indigotin derivative when treated with acetone and sodium hydroxide solution. One of the isomerides produced in the nitration is sparingly soluble in cold concentrated nitric acid, and advantage can be taken of this fact to isolate it in a pure condition in the following way. 2-Methoxy-3-ethoxysalicylaldehyde (5 grams) is added in small quantities at a time to nitric acid (20 c.c.; d 1.42) at $10-20^{\circ}$ with stirring. Even before all the aldehyde has been added, fine, silky needles begin to separate, and when the reaction is complete the product is cooled to 5° , filtered, and the precipitate dried. This substance weighs 2.4 grams and melts at $113-118^{\circ}$; it crystallises from methyl alcohol in colourless, light needles melting at 118.5° . It yields no trace of an indigotin derivative when treated with acetone and sodium hydroxide solution, and is shown to be identical with 5-nitro-2-methoxy-3-ethoxybenzaldehyde (p. 1588) by the method of mixed melting points.

5-Nitro-2-methoxy-3-ethoxybenzaldehyde undergoes no change of colour or melting point when exposed in pure acetone solution for twenty-five hours to ultra-violet rays from a powerful mercury lamp. On the other hand, the well washed nitration product (m. p. 85°) obtained by precipitation with water rapidly becomes greenish-blue when exposed to ultra-violet rays under the same conditions.

When the nitration product (m. p. 85°) is oxidised with potassium permanganate solution, only two acids can be isolated. They are separated by crystallisation from water, the less soluble consisting of needles melting at 177° and identical with 5-nitro-2-methoxy-3-ethoxybenzoic acid (p. 1589). The more soluble acid melts at 157.5° and is apparently identical with the lower-melting acid obtained in the nitration of 2-methoxy-3-ethoxybenzoic acid (see below). Since the nitration product of 2-methoxy-3-ethoxybenzaldehyde can be partly converted into an indigotin derivative, and has been shown above to consist partly of 5-nitro-2-methoxy-3-ethoxybenzaldehyde, and since, on the other hand, the nitration

product can be converted by oxidation into two acids only, there can be little doubt that the more soluble acid melting at 157.5° is 6-nitro-2-methoxy-3-ethoxybenzoic acid. Conclusive evidence of the constitution of this acid will shortly be advanced.

2-Methoxy-3-ethoxybenzoic Acid (XXIII).—This acid is not formed in good yield from the corresponding aldehyde by oxidation with the theoretical quantity of potassium permanganate in water or acetone, a considerable quantity of unchanged aldehyde being left. The following procedure is fairly satisfactory. 2-Methoxy-3-ethoxybenzaldehyde (5 grams), suspended in boiling water (40 c.c.) containing 8 grams of potassium carbonate, is gradually treated with a hot solution of 5 grams of potassium permanganate in 50 c.c. of water. The permanganate solution, which is in large excess, is decolorised in about half an hour, although some unchanged aldehyde is still present, as is shown by the pungent smell of the hot liquid. The reaction liquid is filtered hot, and the filtrate cooled and kept, when a small amount of unchanged aldehyde separates. This is filtered off and the clear solution acidified with hydrochloric acid, whereupon the desired acid crystallises out in a yield of 3.5 grams. 2-Methoxy-3-ethoxybenzoic acid consists of sparkling, colourless, compact crystals melting at 59° , and moderately soluble in cold water (Found: equivalent = 194. $C_{10}H_{12}O_4$ requires equivalent = 196). This acid has a remarkably low melting point, which is not altered by repeated crystallisation.

Nitration of 2-Methoxy-3-ethoxybenzoic Acid.—As shown in the course of some preliminary experiments, the nitration of 2-methoxy-3-ethoxybenzoic acid results in the formation of two mononitroderivatives which differ considerably in their solubility in water and in dilute alcohol, and still more in their rate of separation from water. After various experiments on the latter property, it was found that a rough estimation of the amounts of the two isomerides may be carried out thus: 2-Methoxy-3-ethoxybenzoic acid (20 grams) is dissolved in concentrated nitric acid (20 c.c.; $d\ 1.42$), the temperature being maintained between 15° and 20° . After a few minutes the nitrated acid begins to separate in needles and the nitration mixture is immediately thrown into 150 c.c. of cold water and filtered from the precipitated acid at once. The thick, apparently amorphous precipitate, which is, however, crystalline under the microscope, is well washed with water and dried at 100° , when it weighs 1.28 grams and melts at $175\text{--}177^{\circ}$ (Found: $N = 5.8$. Calc. for $C_{10}H_{11}O_6N$, $N = 5.8$ per cent.). This acid is identical with 5-nitro-2-methoxy-3-ethoxybenzoic acid as shown by the method of mixed melting points. The filtrate—of which the total volume is 330 c.c.—is kept for twenty-four hours, when colourless
311* 2.

prisms (0.50 gram) melting at 157.5° are gradually formed. The filtrate after concentration in a vacuum to 75 c.c. deposits a mixture of acids melting at $142-157^{\circ}$ and weighing 0.35 gram. This mixture has not yet been completely separated into its constituents. The experiment shows, however, that in the nitration of 2-methoxy-3-ethoxybenzoic acid the nitro-group chiefly enters the position meta with respect to the carboxyl group.

6(1)-Nitro-2-methoxy-3-ethoxybenzoic Acid (XXIV) melts at 157.5° and is easily distinguished from the isomeride occurring with it, both by its greater solubility in water and alcohol, and also by its appearance. It is beautifully crystalline, some of the prisms being half a centimetre in length, and hence this acid is easily differentiated from the isomeric 5-nitro-2-methoxy-3-ethoxybenzoic acid, which consists of minute needles. 6-Nitro-2-methoxy-3-ethoxybenzoic acid (Found: equivalent = 240. $C_{10}H_{11}O_6N$ requires equivalent = 241) is apparently identical with the more fusible acid of the two formed by the oxidation of the nitration product of 2-methoxy-3-ethoxybenzaldehyde (p. 1591).

Bromination of 3-Ethoxysalicylaldehyde.

The bromination of 3-ethoxysalicylaldehyde with the calculated quantity of bromine in acetic acid solution does not proceed smoothly, owing to the formation of considerable amounts of a colourless, crystalline substance melting above 250° . This product is sparingly soluble in acetic acid, methyl alcohol, or acetone, but can be conveniently recrystallised from ethylene dibromide. The sparing solubility and high melting point indicate that this substance is an anhydro-aldehyde (or a bromine derivative) of the type investigated by Rupp and Beyer (*loc. cit.*, p. 379). The formation of this substance can be entirely avoided by carrying out the reaction in the following way: 3-Ethoxysalicylaldehyde (3 grams) is dissolved in glacial acetic acid (25 c.c.) to which 5 grams of powdered, freshly fused sodium acetate have been added. The suspension is continually stirred and gradually treated with bromine (30 grams) in glacial acetic acid (6 c.c.), the temperature being maintained between 10° and 20° . The product is poured into water and the solid collected and crystallised from alcohol, from which 2.5 grams of the pure bromine derivative separate.

5-Bromo-2-hydroxy-3-ethoxybenzaldehyde consists of yellow needles melting at 94° , very soluble in hot and sparingly soluble in cold alcohol. The alcoholic solution gives a blue coloration with ferric chloride solution, and a red, crystalline hydrazone with an aqueous alcoholic solution of *p*-nitrophenylhydrazine hydrochloride.

5-Bromo-2-methoxy-3-ethoxybenzaldehyde is produced in almost quantitative yield by methylating the above phenolic substance with methyl sulphate and sodium hydroxide solution in methyl-alcoholic solution. It is readily soluble in hot and sparingly soluble in cold ethyl alcohol, from which it crystallises in long, colourless needles melting at 95° (Found: Br = 31.0. $C_{16}H_{11}O_3Br$ requires Br = 30.9 per cent.).

Bromination of 2-Methoxy-3-ethoxybenzaldehyde.—2-Methoxy-3-ethoxybenzaldehyde (3 grams), dissolved in cold glacial acetic acid (20 c.c.), is treated with bromine (3.0 grams) in 4 c.c. of glacial acetic acid. A small amount of heat is evolved, and the temperature is maintained at $10-20^{\circ}$ for three days, when colourless needles separate. The reaction product is diluted with water and the precipitate crystallised from ethyl alcohol, when 2.55 grams of 5-bromo-2-methoxy-3-ethoxybenzaldehyde are obtained in colourless needles melting at 95° . The melting point is unaltered when the substance is intimately mixed with the bromomethoxyethoxybenzaldehyde obtained by the methylation of the bromination product of 3-ethoxysalicylaldehyde. Moreover, the bromomethoxyethoxybenzaldehydes formed by both processes give identical mononitro-derivatives.

Nitration of 5-Bromo-2-methoxy-3-ethoxybenzaldehyde.—This substance (0.75 gram) is slowly added to nitric acid (25 c.c.; d 1.42) and complete solution is finally attained by warming to 35° . The nitration mixture after standing half an hour is poured into water; the product crystallises from alcohol in very pale yellow needles melting at 128° (Found: N = 4.4. $C_{16}H_{10}O_3NBr$ requires N = 4.6 per cent.). This nitro-aldehyde, when treated with acetone and sodium hydroxide in the way described on p. 1585, is rapidly and almost completely converted into a magnificently coloured indigotin derivative.

The author has pleasure in acknowledging his indebtedness to Professor W. H. Perkin, F.R.S., for a supply of 3-ethoxysalicylaldehyde, and to the Ramsay Memorial Fund.

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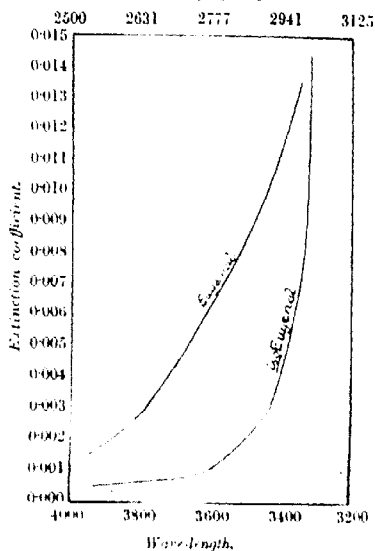
[Received, April 30th, 1923.]

CLXXVIII.—*The Ultra-violet Absorption Spectra of Eugenol and isoEugenol.*

By GARTHA THOMPSON.

In a paper by Crymble, Stewart, Wright, and Glendinning (T., 1911, 99, 451), it is stated that "of two isomeric substances containing two or more double bonds, the compound the molecule of which contains the longest chain of conjugations will have the greater absorptive power in the region of the spectrum above that in which any absorption bands make their appearance."

FIG. 1.
Oscillation frequency.



The method used by these workers was, however, not such as to enable a quantitative statement of the absorbing powers to be made. The following work was undertaken with the view of obtaining figures for this property of eugenol and iso-eugenol.

The apparatus consisted of a Hilger quartz spectrograph, size E₂ (formerly known as size c), a Lewis photometer (T., 1919, 115, 312) and a condensed spark between nickel-steel electrodes.

In order to study the general absorption, solutions of known and approximately $N/20$ strength of eugenol and isoeugenol were made with absolute alcohol, and the effect of absorption by the alcohol was eliminated by placing an absorption tube in each of the two paths of light, one being filled with the solution and the other with the pure solvent.

The method of taking the spectrograms was that described by S. Judd Lewis (*Proc. Royal Soc.*, 1916, [B], 89, 327). The experiments were done in duplicate and the curve was drawn through the mean values. In the main, the agreement was quite satisfactory.

The results for wave-lengths 4000 to 3320 are shown in Fig. 1, where extinction coefficients are plotted against wave-lengths; oscillation frequencies corresponding to a few wave-lengths have also been added to facilitate comparison with the former work.

The extinction coefficient is the quantity $\frac{\log I/I'}{cd}$, where I is the initial intensity of the light, I' the intensity after traversing the absorbing solution, c the concentration in milligram-molecules per litre, and d the length of the tube in centimetres.

On examining the plates, it was found that the limits of complete absorption under the conditions of working were 3200 for eugenol and 3300 for isoeugenol. At the wave-length 3300, isoeugenol has therefore the greater absorptive power, as is to be expected from the law quoted above.

When, however, other wave-lengths are considered, it is found that the law by no means always holds good, for, as shown in Fig. 1 and Table I, in the region 4000 to nearly 3300 eugenol and not iso-

TABLE I.

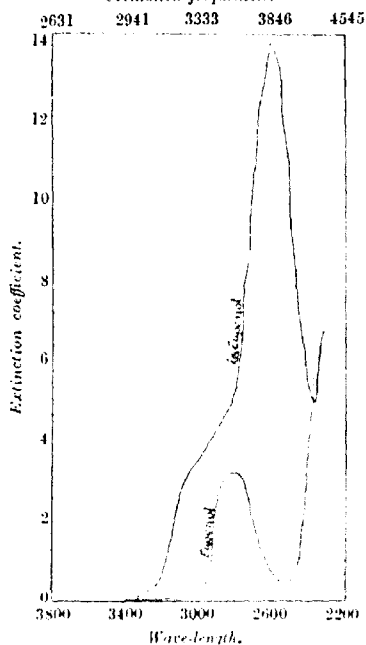
Extinction coefficient.				Extinction coefficient.			
Wave-length.	Eugenol.	isoEugenol.	Eugenol.	Wave-length.	Eugenol.	isoEugenol.	Eugenol.
*3100	0.06	2.70	0.02	3475	0.0093	0.0024	3.88
*3300	0.01	0.20	0.05	3500	0.0087	0.0021	4.43
3325	0.0141	0.0120	1.17	3525	0.0081	0.0019	4.26
3350	0.0133	0.0066	2.01	3550	0.0075	0.0016	4.69
3375	0.0122	0.0051	2.39	3575	0.0069	0.0014	4.93
3400	0.0111	0.0041	2.71	3600	0.0063	0.00125	5.04
3425	0.0104	0.0033	3.15	3625	0.00575	0.00115	5.00
3450	0.0098	0.0028	3.50	3650	0.00525	0.0010	5.23

* The extinction coefficients for these wave-lengths are taken from Fig. 2; and those for the region 3325 to 3650 from Fig. 1. As Fig. 1 is on a very much larger scale than Fig. 2, the values taken from the former curves are much more accurate than those taken from Fig. 2.

eugenol has the greater absorptive power; it is obvious, therefore, that the curves must cross. Since this is so, caution is necessary in applying the Crymble, Stewart, Wright, and Glendinning rule;

in the case of eugenol and isoeugenol, it applies only at wave-lengths between 3320 and 2380, but does not do so in the other regions of the spectrum studied, although these are even more remote from the region of selective absorption than that considered by the former workers.

FIG. 2.
Oscillation frequencies.



The bands were also photographed, with the results shown in Fig. 2 and Table II. In order to obtain these, very much weaker

TABLE II.

	Eugenol.		IsoEugenol.	
	Crymble & co-workers.	Present work.	Crymble & co-workers.	Present work.
Wave-length of head of band.	2830	2820	?	2610
Wave-length of foot of band.	2520	2530	2400	2370

solutions were necessary; concentrations of approximately 0.0005% being required in the case of eugenol and 0.00005% in the case of isoeugenol.

The absorption is in the main very much greater for *isoeugenol* than for *eugenol*; this is particularly noticeable in the region of selective absorption.

As shown in Fig. 2, the curves cross at wave-lengths 3320 and 2380 and therefore at both ends of the spectrum *eugenol* has the greater absorptive power.

The density of the *eugenol* and *isoeugenol* was d_4^{20} 1.0746 and 1.0897, respectively. The figures were obtained after the samples had been distilled under reduced pressure; both substances were nearly colourless. Water was proved to be absent by means of anhydrous copper sulphate.

Summary.

The absorptive powers in terms of extinction coefficients have been found for *eugenol* and *isoeugenol* in the region 4000 to 2300, and the ratio of these powers has been calculated over the region 3100 to 3650.

It has been shown that the rule connecting absorptive power and number of conjugations may be reversed in certain portions of the spectrum, although these portions may be far removed from those in which selective absorption occurs.

The selective absorption of these compounds has also been studied and the effect of the number of conjugations has been found to be particularly great in this region.

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[Received, April 10th, 1923.]

CLXXIX.—*The Properties of some Silver Organosols.*

By JOHN KENNETH GILES and CYRIL SEBASTIAN SALMON.

COMPARATIVELY little is known about the stability and constitution of colloidal solutions in non-aqueous dispersion media. This is due largely to the fact that so many of the systems studied have been of unknown chemical constitution, and that where more simple systems such as metallic alcosols have been investigated sufficient attention has not been directed to the conditions obtaining during the formation of the sol. In most cases, quite large quantities of unknown impurities have been present.

The stability of hydrosols has been shown to be due either to some process analogous to ionisation (the proteins, soaps, etc.), to the adsorption of ions from an electrolyte present in the system (Lottermoser's silver halide sols), or to some process which may be considered intermediate between the two. The investigation

described in this communication is an attempt to determine how far the stability of silver organosols is due to such phenomena.

Silver sols in alcohol have been investigated to a considerable extent. The method of preparation most frequently used has been the arc dispersion method, the presence of reagents necessary for a reduction method thus being avoided. On the other hand, a certain amount of decomposition of the medium is inevitable. Carbon and tarry impurities which have an unknown effect on the stability of the sol are always produced, sometimes in considerable quantities. Svedberg ("Formation of Colloids," p. 25) has carried out an extensive investigation of this method. According to one arrangement of his, the arc was protected by enclosing it in a small quartz tube, the silver vaporised in the arc being carried in a stream of nitrogen into the alcohol which surrounded the tube. The decomposition of the medium was undoubtedly reduced by this device; but a new impurity was introduced, silica from the protecting tube being vaporised by the arc and carried into the dispersion medium. As much as 40 per cent. of the disperse phase in one dispersion was silica. Another impurity probably present was rubber. The quartz tube was held in position by rubber tubing. Some rubber from this was almost certainly extracted by the alcohol or other solvent, such having been found to be the case during preliminary experiments in this investigation.

Silver alcoseols have been obtained by other methods giving purer products, still, however, containing unknown impurities. Thus Svedberg (*op. cit.*, p. 80; *Kolloid Z.*, 1910, **6**, 129) has obtained silver alcoseols by electrolysis and with the use of X-rays. Nordenson (*Kolloid Z.*, 1911, **7**, 91) has shown that in all these cases an intermediate compound is formed between the silver and the alcohol. The sol therefore always contains this unknown compound.

Burton ("Physical Properties of Colloidal Solutions," p. H8) prepared sols of various metals in alcohol and ethyl malonate, using the arc dispersion method. His sols were probably rather impure.

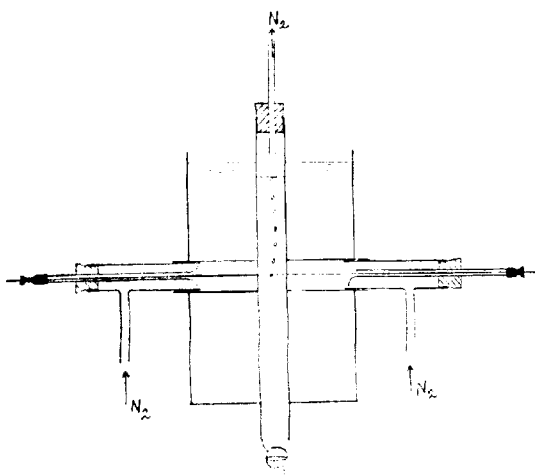
From the work of these investigators it appears probable that stable silver sols cannot be prepared in the pure state, and that, as in hydrosols, the presence of some stabilising agent is essential.

The first object of the investigations here recorded was to determine the nature and concentration of the stabilising agents necessary to give stable sols. Before doing so, in view of the nature of the apparatus used by Svedberg, it was thought advisable to confirm Burton's results as to the instability of pure silver alcoseols.

The apparatus used, shown in the figure, is a modification of Svedberg's enclosed arc apparatus. In this case, neither the arc nor the alcohol comes into contact with anything but silver. Two

silver tubes are soldered together, one in front of the other in the form of a cross, their interiors communicating through a small hole. This cross was soldered to a cylindrical cooling jacket as shown. Two brass T-pieces fit tightly in the ends of the horizontal silver tube. Glass tubes carrying silver wires are fixed inside these T-pieces by rubber bungs. The vertical silver tube is fitted at the bottom with a brass tap, silvered inside, and at the top with an ordinary cork and outlet tube. The nitrogen is led in at the side tubes of the brass T-pieces, passes through the small hole in the two silver tubes, carrying the silver vapour with it, and bubbles up through the alcohol, which is placed in the vertical silver tube.

FIG. 1.



The apparatus was operated by hand: about 6 amperes and 60 volts were used.

Having been prepared in this apparatus, the sol was run out into a specially cleaned test-tube, and observations of its stability were made for about a week. A large number of sols were prepared with absolute alcohol, aqueous alcohol, and alcohol containing various slight additions as dispersion media.

In absolute alcohol, no stable sols were obtained. Burton's results thus being confirmed. The addition of about 15 per cent. of water before dispersion resulted in practically every case in the production of a stable sol. It is impossible to ascertain with greater accuracy the concentration of water necessary to confer

stability, since it is extremely difficult to distinguish between a slowly settling precipitate and a moderately stable sol. The criterion of stability employed was the absence of sedimentation after two days. Stability also depends on other uncontrollable conditions, for example, concentration. The percentage of water is quite large and the mechanism causing stability is probably the same as in ordinary aqueous sols and is ionic in nature.

In water as solvent, the most efficient stabilising ions are the hydrogen- and the hydroxyl-ion. The effect of small additions of acid or alkali was therefore investigated. Caustic soda, aniline, chloroacetic acid, and stearic acid were added in small amounts and found to have no effect. Svedberg states (*Nova Acta Soc. Sci.*, 1907, 2, No. 1) that sols of such metals as silver in alcohol can be stabilised by the addition of bromobenzene. The addition of 0.8 per cent. of this compound was found to have no stabilising effect on sols prepared in this apparatus. The stabilising effect obtained by Svedberg was probably due to decomposition of the bromobenzene, some compound of silver being formed.

From this it appears that the ions most effective in stabilising aqueous colloids have no corresponding effect in alcohol; also, that the effect attributed to bromobenzene is not real. On the other hand, in preliminary experiments it was found that when the solvent came in contact with rubber stoppers or tubing, stable sols resulted. This effect was quite definitely shown to be due to the presence of rubber, thus proving that these sols can be protected by even small quantities of colloids of the emulsoid type.

Silver Sols in Stearic Acid.

As a result of the preparation of certain sols by the arc method Burton (*op. cit.*, p. 151) considered that only substances containing a mobile hydrogen atom could give stable sols of such metals as silver. He suggested using organic acids, but did not carry the investigation any further. Assuming his view to be correct, it appeared to the authors that the most convenient substance to use would be an acid of high molecular weight. An attempt was therefore made to prepare silver sols in stearic acid. The apparatus already described was not found convenient for this purpose. If a sol of silver in stearic acid can exist, it should be formed by reduction of silver stearate in stearic acid with hydrogen—an extension of Kohlschütter's method of preparing silver hydrosols. This method is superior to an arc dispersion method, as decomposition of the medium is prevented.

Preliminary experiments using silver oxide in place of silver stearate indicated that a sol was formed. Reduction took place

slowly at 100° and rapidly at 180° , a red liquid being formed in each case. Ultramicroscopic examination of this red substance showed the presence of a large number of fine particles. In all subsequent work, silver stearate was used. It was prepared from silver nitrate and stearic acid by double decomposition in alcoholic solution. In the latter part of the work, ammoniacal silver nitrate was used. The percentage of silver in the silver stearate was found to be 27.50, compared with a calculated value of 27.58.

When prepared from pure stearic acid, silver stearate is colourless and stable to light. Impure stearic acid gives a product which rapidly turns violet on exposure to light. Below 100° , silver stearate is almost insoluble in stearic acid. Above 100° , the solubility increases rapidly; thus, at 83° and at 180° , the solubility is about 0.005 per cent. and about 50 per cent., respectively.

Reduction with Hydrogen.

When hydrogen was passed through a solution of silver stearate in stearic acid at 180° , the solution rapidly turned dark red with a beautiful purple or blue sheen, and also began to froth. After hydrogen had been passed for some time, the colour of the sol changed from red to dirty mustard colour and finally became grey. This grey mixture settled completely when the current of hydrogen was stopped.

It seemed probable that the sol of silver in stearic acid is stabilised by silver stearate, and becomes unstable when the last trace of this is reduced. To test the accuracy of this hypothesis, analyses were made to determine the course of the reduction. Portions of the sol were removed at intervals and weighed, the stearic acid was extracted with hot absolute alcohol, and the mixture of silver stearate and silver weighed in a Gooch crucible. The total silver was then estimated by solution in nitric acid and titration with ammonium thiocyanate. When silver stearate is dissolved in stearic acid at 180° , the solution turns somewhat orange. It was thought that this might indicate some decomposition of the silver stearate, but an analysis of such a solution showed the presence of 99.5 per cent. of the quantity of silver stearate dissolved, and therefore very little decomposition had taken place.

The results of one reduction experiment are as follow :

Stearic acid, 40 grams; silver stearate, 2 grams; temperature 180° .

Time (hours)	5	10	16	23.5
% Ag reduced	84.9	86.2	91.2	100

After twenty-three hours, a change was observed in the sol; the colour was grey and frothing had ceased. After twenty-four hours,

the stearic acid, when solidified, was as white as the original stearic acid. These results indicate that a very small amount of silver stearate is sufficient to stabilise the sol, but that this small amount is essential. Very much more concentrated sols than this can be obtained. One was prepared which contained 10 per cent. of free silver.

Electrical Condition of the Particles.

As there now seemed no doubt that the red mixture did consist of a silver sol in stearic acid, experiments were made to determine if the particles were electrically charged and, if so, the sign of the charge. Four cataphoresis experiments were carried out at about 80°. Only slight and variable changes in the level of the sol were observed. In order to increase any slight effect that might have been produced, a much smaller U-tube was then used, the distance between the electrodes being only 6 cm. This again gave a negative result.

As no motion was observed in the cataphoresis experiments, an attempt was now made to find if the medium and the sol would conduct at all. It was found at once that the conductivity was far too low to be measured by the method ordinarily used for aqueous solutions. A direct-current method employing a mirror galvanometer was therefore used. With an *E.M.F.* of 200 volts, measurable although very small deflections were obtained. The specific conductivities of pure stearic acid, of a solution of silver stearate in stearic acid, and of the sol were measured and found to be of the same order, about 2×10^{-14} rec. ohm.

Edser ("Fourth Report on Colloid Chem.," p. 313) examined two colloidal solutions in non-conducting media, rust in paraffin and stannic oxide in toluene, and observed no cataphoresis. He assumed, therefore, that the particles were uncharged. This does not necessarily follow. According to Helmholtz (Memoir of the London Physical Soc., 1888), cataphoresis and endosmosis can only occur in a liquid which conducts electricity. If charged particles, suspended in an insulating medium, are subjected to an electric field, a displacement of the components of the double electric layer will take place; but it will stop at a point where the attraction by the external field is balanced by the attraction between the two layers themselves. The fact therefore that a sol does not show cataphoresis does not prove the absence of an electric charge. If the two electrically charged layers are perfectly symmetrical, no displacement at all will take place when the electric field is applied. It is also possible that a double electric layer might be formed, the two charges residing in the extremities of a polar molecule such as silver stearate. Conductivity determin-

ations, on the other hand, show definitely that if there is any charge it is not due to the adsorption of ions and therefore that the stabilising effect of silver stearate is not similar to that of ferric chloride on a ferric hydroxide sol.

Surface Tension and Viscosity.

As previously mentioned, it was noticed that when a mixture of stearic acid and silver stearate was being reduced with hydrogen, after about five minutes or less a froth of very stable bubbles was formed. This frothing continued until all the silver stearate had been reduced and the sol became unstable. It therefore seemed probable that the silver stearate lowered the surface tension of the stearic acid. Measurements of surface tension were made and it was hoped that if the effect was sufficiently great the surface tension might be measured from time to time during a reduction, and the relation between composition, surface tension, and the stability of the sol investigated. At the same time, it was thought of interest to see if the viscosity of the stearic acid was affected by the presence of silver stearate or silver sol.

The surface tension was determined by the rise in a capillary tube at 138°, this temperature being maintained by means of boiling xylene. The results obtained were:

	Surface tension.	Density.
Stearic acid	22.7	0.8019
Stearic acid + 2% silver stearate	22.6	0.8070
Silver sol in stearic acid	21.0	(0.8070)

These results show that the presence of 2 per cent. of silver stearate does not appreciably lower the surface tension of stearic acid. No accurate value could be obtained for the sol, owing possibly to the silver being deposited in the capillary tube. A considerable lowering, however, was observed.

The viscosity determinations were made in an ordinary Ostwald viscometer, heated in a bath of the vapour of boiling xylene. The reading for pure stearic acid was first taken and then silver stearate was added to give a 2 per cent. solution. Readings were taken for this solution, which was then reduced in the viscometer with a current of hydrogen, and the time of flow of the sol noted. The following results were obtained:

Temperature 138°	Time of flow (mins.).	Density.	<i>t d.</i>
Stearic acid	179.5	0.8019	144.0
2% silver stearate	183.0	0.8070	147.7
Silver sol	179.0	(0.8070)	144.4

It will be observed that *t d.*, which is proportional to the viscosity, is slightly increased by the addition of 2 per cent. of silver stearate.

This increase, about 3 per cent., is more comparable with the increase produced by crystalloids than by colloids such as soap in water. The silver sol is seen to have practically the same viscosity as the pure medium.

Stability of the Silver-Stearic Acid Sol to Change of Solvent.

The behaviour of the sol when its dispersion medium was changed from stearic acid to a solution of stearic acid in various solvents was investigated. The following results were obtained when approximately equal weights of the sol were dissolved in the same volume of the solvents :

Solvent.	
Paraffin wax	Quite stable.
Ligroin)	Stable. A slight black deposit gradually formed. Stability greater than 14 days.
Hexane)	
Toluene)	
Benzene	Fairly stable. Settled completely in a week. Black ppt.
Xylene	Settled completely in 1 day. Black ppt.
Ethyl alcohol	Settled in a few minutes. Black ppt.
Amyl alcohol	Settled in 1 day. Red ppt.
Amyl acetate	Deep red sol. Very opaque and stable. Slight black deposit after 10 days. This sol was found to be negatively charged.
Acetone	The sol at first appeared quite unstable and a black deposit formed. After about 4 hours, this coagulation stopped and the remaining sol became quite stable. It was found to be negatively charged.
Ether	Unstable. The sol settled completely in 1 day. The ppt. was white.

These results are discussed in the conclusion.

Coagulation.

The sol coagulated when heated strongly with sodium chloride. Sodium sulphate had no such coagulating effect. This seemed to suggest that the precipitation was due to a reaction between the salt and the silver stearate giving silver chloride and sodium stearate. Hydrogen chloride gas was found to coagulate the sol much more quickly and at a lower temperature than sodium chloride. Analyses of the sol before and after coagulation indicated that the hydrogen chloride rapidly attacked first the silver stearate and then, gradually, the free silver. It also quickly coagulated a solution of the sol in benzene at room temperature.

Silver Sols in other Dispersion Media.

The method of preparing a colloidal solution of silver in an acid which proved successful in the case of stearic acid was tried

with other fatty acids in order to find out what effect variation in the length of the carbon chain has on the stability of the sol.

Acetic Acid.—Special care was taken to dry the acetic acid. After being purified by partial solidification, it was heated for some time with a few drops of acetic anhydride and distilled directly into a flask containing silver acetate. A current of hydrogen was then bubbled through the mixture. Reduction took place gradually at 80°. A brown stain was formed on the glass, and a coarse suspension in the liquid. It was observed that sols could be formed, although they were not stable, by heating acetic acid with silver acetate; the mixture, which was colourless initially, became yellow, then reddish-brown, and finally green. At whatever stage the action was stopped the sol rapidly coagulated.

Valeric, n-Octoic, Lauric, Palmitic, and Margaric Acids.—The silver salts of these acids were prepared by the action of an ammoniacal solution of silver nitrate on an alcoholic solution of the acid (Found: Ag = 51.81; 42.92; 35.14; 29.2; 28.4 per cent. for the respective silver salts in the order given above).

In each case, a current of hydrogen was passed through a mixture of the acid with a small quantity of the silver salt heated at 100°; a reddish-brown sol was formed, most rapidly in the case of valeric acid. When an intensely coloured sol had been formed (two minutes for valeric, ten minutes for *n*-octoic, thirty to sixty minutes for the other acids), the current of hydrogen was stopped and the sol kept at 100° for observation of stability. The sol in valeric acid showed definite signs of coagulation in five minutes and was completely coagulated in about ten minutes. In the case of *n*-octoic acid, the first signs of coagulation appeared in ten minutes, and it was complete after twenty-five minutes. The sols in lauric, palmitic, and margaric acids were quite stable and showed no signs of coagulation. Frothing was observed during the production of each of the sols as in the case of stearic acid.

It was desired to find the effect of substituting a phenyl group for the fatty hydrocarbon chain. A suspension of silver benzoate in benzene was therefore treated with hydrogen, benzoic acid not being suitable as a dispersion medium. A red sol was formed. It coagulated, however, completely in about an hour.

The effect of the presence of two carboxyl groups was investigated in the case of sebacic acid. No sign of sol formation was observed.

Conclusion.

From a consideration of previous work on this subject and of the results of this research, it seems that, as a rule, a stable organo-

sol can be formed only when there is present, besides the dispersion medium and the disperse phase, a polar compound containing radicles similar to those in each of the two phases.

First with regard to alcohol: stable alcosols of zinc, tin, and lead have been prepared by Burton (*op. cit.*, p. 147), but he could not obtain stable alcosols of silver, gold, or platinum. It seems probable that the positive metals form ethoxides or hydroxyethoxides, whereas the noble metals do not. Again, in both cases in which purer silver alcosols have been prepared—by electrolysis and by illumination of a silver plate in alcohol by ultra-violet light—it has been shown, as already mentioned, that some silver compound is formed.

With regard to silver and stearic acid, the case is quite clear. At one time, the authors were of opinion that in dispersion media in which the molecules were long chains adsorption of these molecules stabilised the sol, no intermediate substance being present. But this is evidently not the case. The presence of a little silver stearate is essential to the production of a stable sol, whilst on its removal the sol becomes quite unstable. This behaviour is comparable in some respects with that of ferric hydroxide hydrosols, for the stability of which a small quantity of a ferric salt is necessary. In this case, the stability is definitely an ionic effect. The colloidal complexes acquire a positive charge, whilst the corresponding negative chlorine ions remain free in the liquid. Conductivity determinations show conclusively that this cannot be the case with the silver-stearic acid sol, and it becomes necessary to postulate a non-ionic mechanism of the stabilising action of silver stearate. The most probable explanation is adsorption by the metallic silver particles and consequent lowering of the surface tension between them and the dispersion medium. The work of Langmuir, Harkins, and others has shown that, at interfaces, polar molecules of the type of stearic acid tend to arrange themselves so that the ends of the molecule are directed towards the phase they more strongly resemble. In the case under consideration, the silver atom would be attached to the colloidal silver particle, whilst the hydrocarbon chain would be extended into the stearic acid. This arrangement would considerably decrease the tendency towards coagulation: each silver particle, being covered with a layer of fatty acid, would behave as a large (associated) stearic acid molecule.

It appears to be an established fact ("Fourth Report on Colloid Chemistry," p. 49) that molecular attraction extends to a considerable distance and that it is not only the contiguous molecule or atom that is affected. We should expect, therefore, that the stability of an organosol of the type silver AgX -dispersion medium

would be dependent on (i) the similarity between X and the dispersion medium, and (ii) the length of the X group.

(i) The results recording the effect of change of medium on the stability of the silver-stearic acid sol illustrate the importance of this factor. Paraffin wax gave the most stable sol. Ligroin and hexane, which still resemble the radicle $C_{17}H_{35}$ quite closely, gave sols nearly as stable. Of the remainder, benzene gave a fairly stable sol, and ethyl alcohol, amyl alcohol, and ethyl ether did not give stable sols. In the cases of acetone and amyl acetate, ionic complications arose and stable, negatively charged sols resulted.

(ii) The effect of this factor is seen in the different stabilities of the sol in various fatty acids. In acetic acid, very transitory sols only were formed. In valeric and *n*-octoic acids, sols were formed which quickly coagulated. In lauric, palmitic, margaric, and stearic acids, stable sols were formed. Benzene and silver benzoate gave a sol the stability of which was intermediate between those of the *n*-octoic and the lauric acid sols.

It is impossible to say definitely whether in these solutions the silver salts are molecularly dispersed or are present in the colloidal state. They apparently show a definite solubility, which is a characteristic of true solutions, but, on the other hand, concentrated solutions show a tendency to gel on cooling. Very possibly sols are only formed when the solubility of the silver salt is suddenly reduced by cooling. The stabilising action of the salts runs parallel with the molecular weight and therefore with the tendency to form colloidal solutions, but in the very small concentration necessary for stability it is probable that they are present as crystalloids as in the case of aqueous soap solutions.

It is interesting to consider one case of protection in the light of this hypothesis. Very stable silver, gold, and platinum organosols can be made by a method described by Amberger (*Kolloid Z.*, 1915, **11**, 97, 100): A concentrated solution of silver nitrate is mixed with lanoline, and caustic soda added. The mass is left exposed to daylight for some time, when it will dissolve in an organic solvent to give a silver organosol. Lanoline consists chiefly of cholesterol, $C_{27}H_{45}OH$, a complex alcohol containing a terpene ring and the group $>C=CH_2$; on oxidation, this yields various complex acids. In the preparation of the sol, the silver salts of these acids are formed by the oxidising action of silver oxide. They are then adsorbed by the free silver which is also produced, the great length of the hydrocarbon residue making it a very efficient stabilising agent. A very large number of protective agents are acids of high molecular weight, for example, the proteins

and their decomposition product, lysalbic acid, so that a great many protective actions may have a similar explanation. Further investigations on this point are in progress, in the course of which it is proposed to study the formation of silver sols in glycerol in the presence of silver mannonate, which, according to the hypothesis outlined above, should be an effective stabilising agent.

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[Received, May 7th, 1923.]

CLXXX.—*The Freezing-point Curve for Mixtures of Potassium Nitrate and Sodium Nitrate.*

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THE earliest systematic investigation of the freezing points of mixtures of sodium nitrate and potassium nitrate appears to be that of Schaffgotsch (*Pogg. Ann.*, 1857, **102**, 293; *Jahresber.*, 1857, 19); later, Carveth (*J. Physical Chem.*, 1898, **2**, 209) examined the ternary system comprising the nitrates of sodium, potassium, and silver and incidentally redetermined the freezing-point curve for the binary mixtures now under consideration. Both sets of data are plotted in Fig. 1; and it will be observed that the curves obtained by joining the points of each set are fairly smooth curves of similar form.

Nevertheless, Schaffgotsch and Carveth agreed in assuming that their results should be represented by nearly straight lines drawn among the points on either side and meeting in a eutectic point, and that the eutectic mixture consisted of practically pure sodium nitrate and potassium nitrate.

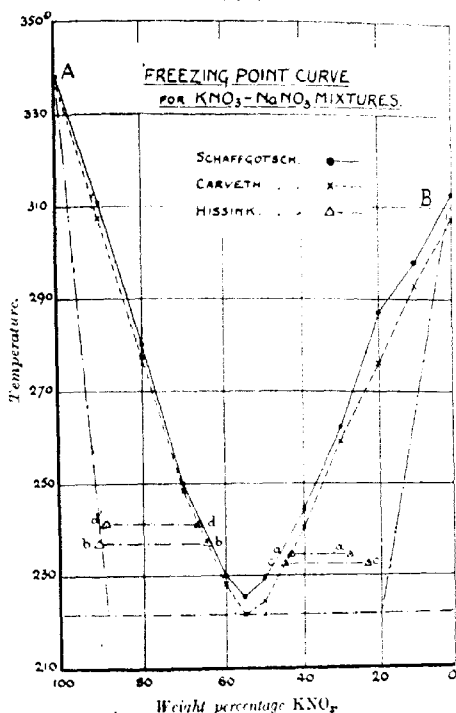
Hissink, in the course of a general study of mixed crystals (*Z. physikal. Chem.*, 1900, **32**, 537), using the vacuum filtration method of Van Eyk (*ibid.*, 1899, **30**, 432), separated and analysed the solid in equilibrium with certain liquid mixtures of sodium and potassium nitrates. His results, recalculated to a weight-percentage basis, indicate that solids *a'*, *b'*, *c'*, *d'*, containing, respectively, 28.4, 90.8, 23.6, and 89.3 per cent. of potassium nitrate, are in equilibrium with liquids *a*, *b*, *c*, *d*, containing, respectively, 43.3, 64.25, 44.5, and 66.45 per cent. of potassium nitrate: these points are plotted in Fig. 1.

Hissink, accepting the views of Schaffgotsch and Carveth as to the nature of the freezing-point curve, concluded that the eutectic mixture consisted of two kinds of solid solutions of the limiting

compositions 12 per cent. NaNO_3 and 20 per cent. KNO_3 , determined' approximately by projecting rectilinear solidus curves from *A* and *B* (Fig. 1) through the points *b'*, *d'* and *a'*, *c'* upon the eutectic temperature line.

It is remarkable that, although sodium nitrate crystallises in the rhombohedral system, in which all the other alkali nitrates, thallous

FIG. 1.



nitrate, and silver nitrate also crystallise, no case has hitherto, been known in which sodium nitrate forms a complete series of solid solutions with any one of the other nitrates. Attention has recently been directed to this anomaly by Early and Lowry (T., 1922, 121, 967).

The experimental work described in the present communication affords evidence that the nitrates of sodium and potassium do, in

fact, form a continuous series of solid solutions at all temperatures above 130°, the transition point of potassium nitrate.

EXPERIMENTAL.

The freezing points of a series of synthetic mixtures of pure sodium nitrate and potassium nitrate were determined by the cooling curve method. Purification of the salts was effected by six successive recrystallisations from pure water, the mother-liquor in each crystallisation being removed as completely as possible by suction. Before weighing, the salts were powdered and dried at 120° for at least three hours; it seems reasonable to assume that any residual impurity could have had no effect on subsequent measurements.

For the measurements of Series I and II the heater used was made by winding two layers of wet asbestos paper on the lower 12 cm. of a 3 cm. diameter Jena-glass test-tube, winding 10 metres of No. 28 B. & S. nichrome wire spirally over this, and insulating the whole with three thicknesses of wet $\frac{1}{8}$ -inch asbestos millboard. On drying, first at atmospheric temperature and finally by passing a small current through the winding, the heater was so consolidated that the test-tube could be removed and reinserted as desired. The heater used for Series III and IV was similar, save that the melt was contained in an inner tube separated from the heater tube by an annular air-space.

As a moderate degree of accuracy only was sought, temperatures were determined with a mercury-in-glass thermometer, nitrogen filled, having a range of - 10° to 400° and graduated in degrees. This was calibrated (1) by direct comparison with standard, nitrogen-filled, mercury thermometers which had themselves been twice calibrated by the Reichsanstalt, using baths of water, vaselin, and Rose's fusible metal, and (2), more accurately, by using it to determine the apparent boiling points of pure water, aniline, nitrobenzene, bromonaphthalene, and benzophenone, the thermometer being, of course, completely immersed in the vapour.

The correction for the exposed stem could not well be determined by the ordinary method using a single secondary thermometer, because clearly that part of the stem within the test-tube was at a much higher temperature than and had a different temperature gradient from the part exposed to air outside the test-tube. Two secondary thermometers were therefore employed, placed three-quarters of the way down the enclosed and the exposed portion of the stem respectively, and the correction, s , was calculated separately for each part of the stem. According to the usual expression, $s = a n (T - t)$, where a is the coefficient of expansion of mercury in glass, n is the number of degrees of exposed stem, T is the

temperature registered, and t is the mean temperature of the exposed stem indicated by the secondary thermometer. There is some doubt as to the best value of a , but in the present work that of Thorpe (T., 1880, 37, 160), $a = 0.000143$, is used. It seems probable that the correction thus determined is not in error by more than the error of reading, which does not exceed 0.2° .

The freezing point of each pure substance or mixture was determined by fusing about 20–30 grams in the apparatus above described, clamping the thermometer eccentrically in the tube, with the bulb and a few millimetres of the stem immersed in the melt, and reducing the heating current until the temperature of the bath fell slowly, the melt being meanwhile stirred by rotating the tube. Readings of time and temperature were then taken which, when plotted, permitted an accurate location of the temperature at which cooling was arrested. It was found that observation of the temperature at which rotation of the tube was no longer possible gave a sharp determination of the setting point, in agreement with that deduced from the cooling curve.

The freezing point of one of the pure salts having been thus determined, successive weighed portions of the other were added and the freezing point similarly determined after each addition.

Attempts to secure check determinations by the heating curve method were attended by the usual difficulty that the arrest points were ill-defined, and were abandoned because, with pure potassium nitrate or any mixture containing more than about 30 per cent. of this salt, the tube invariably cracked at about 130° . This is probably due to the transition from the orthorhombic to the rhombohedral modification which occurs at 129° (Wallerant, *Compt. rend.*, 1905, 130, 264) with a pronounced crackling noise and a considerable increase in volume. At the same time, it is not very clear why the converse transition, which takes place on cooling, does not by shrinkage create a space sufficient to permit the expansion on heating.

In the freezing-point determination any difficulty from this cause was avoided by remelting the contents of the tube before they had cooled to 130° , removing the thermometer, and inclining the tube so that the melt nowhere occupied the full diameter and so was free to expand when remelted.

Four series of determinations were made. Series I and III began with pure potassium nitrate, Series II with pure sodium nitrate, and Series IV with a mixture containing 71 per cent. of sodium nitrate; and each was carried well past the minimum point. The whole of the data, including the actual calibration and exposed stem corrections, are given in Table I and the corrected freezing

TABLE I.
Experimental Data for Freezing Points of Mixtures of Sodium
Nitrate and Potassium Nitrate.

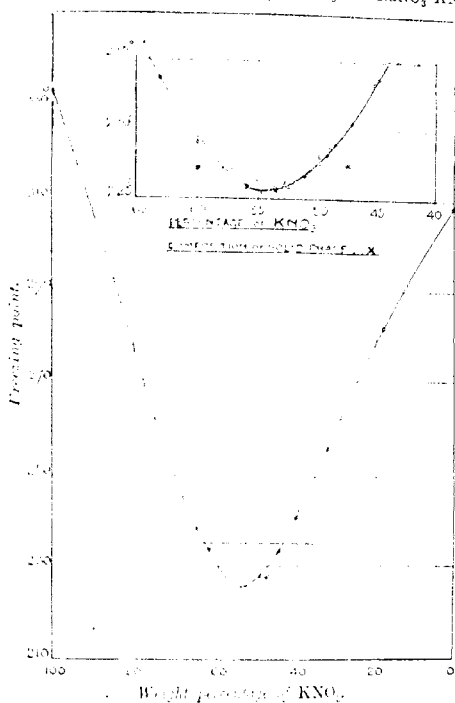
		Corrections.				Corrected m. p.
% KNO ₃	% NaNO ₃	Observed m. p.	Cali- bration.	Exposed stem.	Total.	
Series I.						
100.0	0.0	320.8°	2.3°	9.5°	11.8°	332.6°
90.8	9.2	297.6	2.2	8.1	10.3	307.9
77.6	22.4	261.0	2.0	5.9	7.9	268.9
68.5	31.5	238.5	1.85	4.6	6.5	245.0
65.0	35.0	232.0	1.82	4.3	6.1	238.1
59.1	40.9	223.2	1.81	3.8	5.6	228.8
56.1	43.9	220.7	1.8	3.7	5.5	226.2
55.7	44.3	220.3	1.8	3.6	5.4	225.7
54.8	45.2	220.0	1.8	3.6	5.4	225.4
53.5	46.5	220.2	1.8	3.6	5.4	225.6
52.7	47.3	220.5	1.8	3.6	5.4	225.9
51.2	48.8	221.0	1.8	3.7	5.5	226.5
50.1	49.9	222.0	1.8	3.7	5.5	227.5
49.4	50.6	222.5	1.81	3.8	5.6	228.1
Series II.						
57.2	42.8	221.6	1.82	3.7	5.5	227.1
56.4	43.6	221.1	1.82	3.7	5.5	226.6
55.25	44.75	220.9	1.81	3.7	5.5	226.4
53.8	46.2	220.5	1.81	3.65	5.5	226.0
52.9	47.1	220.8	1.81	3.7	5.5	226.3
50.8	49.2	221.5	1.82	3.7	5.5	227.0
50.0	50.0	222.4	1.82	3.75	5.6	228.0
49.1	50.9	223.0	1.82	3.8	5.6	228.6
47.2	52.8	224.7	1.82	3.9	5.7	230.4
45.1	54.9	227.1	1.83	4.0	6.2	233.3
32.7	67.3	248.5	1.9	5.25	7.2	255.7
18.1	81.9	273.2	2.03	6.7	8.7	281.9
0.0	100.0	298.5	2.2	8.2	10.4	308.9
Series III.						
100.0	0.0	321.3	2.3	9.5	11.8	333.1
85.0	15.0	282.5	2.1	7.2	9.3	291.8
75.0	25.0	254.5	1.9	5.6	7.5	262.0
63.0	37.0	227.8	1.8	4.1	5.9	233.7
60.0	40.0	223.5	1.8	3.8	5.6	229.1
57.75	42.25	221.7	1.8	3.7	5.5	227.2
55.3	44.7	220.3	1.8	3.6	5.4	225.7
54.7	45.3	220.1	1.8	3.6	5.4	225.5
53.7	46.3	220.5	1.8	3.6	5.4	225.9
52.9	47.1	220.6	1.8	3.6	5.4	226.0
52.2	47.8	220.7	1.8	3.6	5.4	226.1
48.6	51.4	223.2	1.81	3.8	5.6	228.8
43.7	56.3	229.8	1.82	4.2	6.0	235.8
38.0	62.0	239.6	1.86	4.75	6.6	246.2
31.2	68.8	251.7	1.9	5.45	7.3	259.0
Series IV.						
66.9	33.1	235.5	1.86	4.5	6.4	241.9
59.5	40.5	223.4	1.82	3.85	5.7	229.1
56.0	44.0	220.6	1.81	3.7	5.5	226.1
53.7	46.3	220.4	1.81	3.6	5.4	225.8
52.1	47.9	220.9	1.81	3.7	5.5	226.4
50.8	49.2	221.3	1.82	3.7	5.5	226.8
48.0	52.0	223.8	1.82	3.8	5.6	229.4
44.8	55.2	227.8	1.83	4.1	5.9	233.7
38.7	61.3	234.5	1.86	4.7	6.3	240.8
31.2	68.8	251.7	1.9	5.45	7.3	259.0

points are plotted in Fig. 2, the upper part of which shows on a larger scale the curve in the region of the minimum below the dotted horizontal line.

From the continuity of the freezing-point curve, the existence of a complete series of solid solutions is to be inferred, and as this inference is in sharp opposition to the views hitherto held, experi-

FIG. 2.

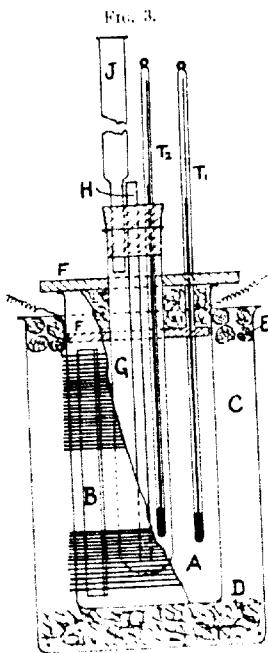
Freezing point composition diagram for the system $\text{NaNO}_3\text{-KNO}_3$.



ments were made to ascertain the composition of the solid phase in equilibrium with molten mixtures the composition of which differed slightly in either direction from that of the mixture of minimum freezing point. Here the chief difficulty is to secure a slow deposition of solid in true equilibrium with the melt and to separate it from the mother-liquor. Whilst a number of methods have been fully described for the separation of solids from solutions with which

they are in equilibrium, little information has been found in the literature as to methods whereby the solid phase can be separated from molten salts. The following plan was therefore adopted.

The apparatus, shown in Fig. 3, comprised a tall narrow beaker, *A*, surrounded by a winding of No. 28 B. & S. nichrome wire which was held, and spaced clear from the walls of the beaker, by asbestos millboard strips *B*, *A* being supported in a larger beaker, *C*, by an asbestos pad, *D*, and a collar of asbestos rope, *E*. The vessel *A* was fitted with a double lid, *F*, of asbestos millboard packed with woolly asbestos, through which passed a thermometer, T_1 , and a 1-inch test-tube, *G*, closed by a cork carrying a second thermometer, T_2 , and two tubes, *H* and *J*, designed to cause circulation of cool air through *G*. The tube *J* was held in a clamp, thus supporting *G* in any desired position. By adjustment of external resistance in the heating circuit, the apparatus could be held at any desired temperature up to about 300° or allowed to cool at any desired rate, whilst the contents could be clearly observed by transmitted light.



In conducting an experiment, about 250 grams of the mixture under investigation were melted in a porcelain dish over a free flame while the apparatus was heated electrically to a temperature some 20–30° above the freezing point of the mixture. Then the melt was poured into *A* and the lid *F* replaced with the tube

G immersed some 5 cm. in the melt.

The apparatus was cooled to within one or two degrees of the freezing point and then the rate of cooling was adjusted to about 0.05° per minute until a fine ring of crystals appeared on *G*, after which the rate of cooling was still further reduced.

After about an hour, the ring of crystals on *G* had grown and a second ring had formed on the walls of the beaker *A* at the free surface of the melt, the total quantity of solid thus deposited being about 2–4 grams. The tube *G* was then raised about 3 cm., and

its withdrawal lowered the surface of the liquid in the beaker by some 1.5 cm., so that the crystals, both on the tube and on the beaker, drained at a temperature practically that of the melt. A second crop of crystals was grown with the tube in its new position, and these in turn were similarly drained by raising the tube again. It was observed that the mass of crystals, before withdrawal from the liquid, was fairly solid and therefore could scarcely have retained after drainage any very large proportion of included mother-liquor.

The tube *G* having been removed, with its adherent samples of the solid phase, samples of the melt were drawn into previously heated glass tubes, in which they afterwards solidified. A second sample of the melt was obtained by crushing the whole mass of solid which remained in *A* on cooling.

Two series of crystallisations, *A* and *B*, were made as above described, starting with mixtures made up to contain approximately 50 per cent. and 58 per cent. of potassium nitrate, respectively. Determinations of potash in the various samples were made gravimetrically by the perchlorate method, and the results, calculated as KNO_3 , are given in Table II.

TABLE II.

Composition of Liquid and Solid Phases in Equilibrium in Fused Mixtures of Sodium and Potassium Nitrates.

		Series A.	Found % KNO_3 .	Mean % KNO_3 .
Liquid phase	(1. Sampled in tubes		59.14; 59.25	59.12
	(2. Sample from bulk		59.01; 59.09	
Solid phase	(3. Upper ring on tube		48.51; 48.90	48.46
	(4. Lower ring on tube		49.07; 48.62	
	(5. Upper ring on beaker		48.15; 47.54	
		Series B.		
Liquid phase	(1. Sampled in tubes		57.57; 57.82	57.73
	(2. Sample from bulk		57.72; 57.90	
Solid phase	(3. Upper ring on tube		58.96; 59.74	59.26
	(4. Lower ring on tube		59.06; 59.11	
	(5. Upper ring on beaker		59.12; 59.54	

Discussion of Results.

Whilst the freezing point data here presented have no claim to any unusually high degree of absolute accuracy, they would appear to constitute a consistent series of observations which merit confidence as a means of determining the *form* of the freezing-point curve. Curves deduced independently from the four series of measurements are practically coincident in the region of the minimum although the errors of weighing are, in this case, additive, and

evidently increase toward the end of each series. For this reason, it is the more significant that all four series agree in showing in the region of the minimum a continuous curve of substantially the same form.

It is evident that this continuity of the curve is entirely incompatible with the view hitherto held that sodium nitrate and potassium nitrate are immiscible, or of limited miscibility, in the solid state, and form a eutectic mixture: it indicates, on the contrary, that the salts form a complete series of solid solutions. A comparison of Figs. 1 and 2 shows that the data now reported are not in serious disagreement with the corresponding data in the earlier work. The nature of the curve has been misunderstood previously, because the points determined were too few to fix it precisely in the region near the minimum, where the curvature changes rapidly, and because the earlier workers evidently assumed that curves so nearly straight and tending together at such an angle as in this case would necessarily meet in a eutectic point; otherwise it is difficult to account for their disregard of the obvious approximation to a continuous curve which is presented by simply joining the points they determined (Fig. 1). This assumption, indeed, seems still to be held rather generally, but it is clearly untenable in view of the results now reported, and it might be profitable to subject some other supposed eutectic mixtures to more rigorous investigation.

Consideration of the form of the cooling curves determined in the present investigation supports the foregoing conclusion. A typical eutectic mixture, for example, bismuth-tin, gives cooling curves showing a sharp arrest at the eutectic temperature as well as at the initial freezing point. The curves for mixtures of potassium and sodium nitrates show no second arrest, whence it is clear that a progressive solidification occurs over the whole range from the initial freezing point to the minimum, at which point the mass of material finally solidifying is very small.

In order to obtain an independent and decisive check on our conclusion, the nature of the solid phase in equilibrium with fused mixtures near the minimum freezing point was determined in the manner above described. If sodium nitrate and potassium nitrate were immiscible or of limited miscibility in the solid state, the pure solid or the limiting solution would separate from any mixture right down to the minimum point, so that the solids separating from solutions of compositions close to, but on either side of, that of the mixture of minimum freezing point would differ widely in composition. The analyses reported in Table II show that the composition of these solids differs very slightly from that of the liquid phase in equilibrium. As this is the case, the inclusion of

considerable amounts of mother-liquor has little effect on the composition, deduced from the analytical data, for the pure solid phase freed from mother-liquor. Even on the rather generous assumption that the crystals contained 30 per cent. by weight of included liquid, the percentage of potassium nitrate in the pure crystals would only differ by about half a unit from that found for the crystals plus mother-liquor. Allowing a still larger correction of, approximately, one unit upon the analytical figures, it may be said with some confidence that the solids in equilibrium with liquid mixtures containing 50.12 per cent. and 57.75 per cent. of potassium nitrate contain, in round numbers, not less than 47.5 per cent. and not more than 60.0 per cent. of potassium nitrate, respectively.

Therefore it is apparent that these solids are neither the pure components nor the solid solutions containing, respectively, 12 per cent. of potassium nitrate and 20 per cent. of sodium nitrate, supposed by Hissink to represent the limits of miscibility of these salts in the solid state.

On the other hand, Hissink's data, having regard to the rather considerable errors by which they are obviously affected, do not preclude a *solidus* curve, of the general form and location indicated by the dotted curve in Fig. 2.

We conclude, therefore, that sodium nitrate and potassium nitrate, at temperatures above 130° , form a continuous series of solid solutions. Below 130° , these solutions change to a porcelain-like mass, owing undoubtedly to the segregation of potassium nitrate in the orthorhombic form. This change may sometimes be delayed; for example, the molten mixtures on glass may form perfectly clear and transparent crystalline films on cooling to room temperature; mechanical disturbance or the addition of moisture then causes the films to become white and opaque. Microscopic examination of the films during this change confirms the foregoing opinion as to its nature.

The melting points of the pure components, determined incidentally in the course of the present work, merit brief comment; they are given below, together with the more important earlier values for these constants.

KNO_3 339° ; 342° ; 338° ; 339° ; 337° ; 333° .

NaNO_3 310.5° ; 314° ; 313° ; 316° ; 308° ; 309° .

The authorities for the respective pairs of values are Persen (*Ann. Chim. Phys.*, 1847, [iii], 21, 329), Braun (*Pogg. Ann.*, 1874, 154, 190), Schaffgotsch (*Pogg. Ann.*, 1857, 102, 293; *Jahresberichte*, 1857, 49), Carnelly (*J. Chem. Soc.*, 1878, 33, 277), Carveth (*J. Physical Chem.*, 1898, 2, 269), and Briscoe and Madgin.

In the present investigation, the salts were carefully purified and

the determination of temperature can scarcely be in error by much more than $\pm 0.5^\circ$, so that the present results, differing little from the earlier data of Schaffgotsch and Carveth, appear to merit confidence.

Summary.

1. The freezing-point curve for mixtures of sodium nitrate and potassium nitrate has been redetermined and found to be continuous, with a fairly sharp minimum at 225.7° and approximately 55 per cent. KNO_3 .

2. Cooling curves for these mixtures exhibit a sharp arrest at the initial freezing point, but show no material arrest at the minimum freezing point.

3. The solids in equilibrium with liquid mixtures near the composition of minimum freezing point are solid solutions differing little in composition from those liquids.

4. It is inferred that sodium nitrate and potassium nitrate, at temperatures above 130° , form a continuous series of solid solutions, and not, as has hitherto been supposed, a eutectic mixture of the pure salts or of solid solutions of limiting composition.

5. The melting points of sodium nitrate and potassium nitrate are found to be $309^\circ \pm 0.5^\circ$ and $333^\circ \pm 0.5^\circ$, respectively.

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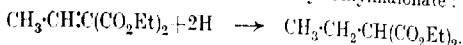
[Received, May 2nd, 1923.]

CLXXXI.—*Reduction of Ethyl Ethylidenemalonate as Affected by Choice of Reducing Agent.*

By LUCY HIGGINBOTHAM and ARTHUR LAPWORTH.

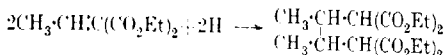
STUDIES of α , β -unsaturated acids and esters which have been in progress in these laboratories have included certain investigations of reduction products of alkylidenecyanoacetic acids. It has been observed that the unsaturated acids, $\text{Ar}\cdot\text{CH}=\text{C}(\text{CN})\cdot\text{CO}_2\text{H}$, made by condensation of aromatic aldehydes, $\text{Ar}\cdot\text{CHO}$, with cyanoacetic acid, are reduced by means of sodium amalgam and mainly to the corresponding saturated acids, $\text{Ar}\cdot\text{CH}_2\cdot\text{CH}(\text{CN})\cdot\text{CO}_2\text{H}$, but that when the corresponding acids derived from aliphatic aldehydes are used the expected reduction products are not obtained, although very ready absorption of hydrogen takes place. In a similar manner, ethyl ethylidenecyanoacetate and ethyl ethylidenemalonate, $\text{CH}_3\cdot\text{CH}=\text{C}(\text{CN})\cdot\text{CO}_2\text{Et}$, are easily reduced by moist sodium amalgam, but the products give no trace of the expected *n*-butyric acid

after complete hydrolysis and elimination of carbon dioxide. These observations seemed the more remarkable inasmuch as ethyl ethylidenemalonate was found to be capable of ready reduction in the cold with hydrogen in presence of colloidal palladium, being almost quantitatively converted into ethyl ethylmalonate:

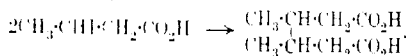


In order to ascertain the probable nature of the abnormal course pursued when moist sodium amalgam is used as reducing agent with these $\alpha\beta$ -unsaturated acids and esters, attention was concentrated on ethyl ethylidenemalonate and it was found that this ester with sodium amalgam gives rise to products of at least two distinct types. The first of these has many of the characters of a β -ketonic ester, and yields on alkaline hydrolysis a volatile ketone from which a crystalline semicarbazone can be obtained; this compound has not yet been isolated in quantities large enough to permit of its full characterisation.

The main type of product obtained by reduction of ethyl ethylidenemalonate by moist sodium amalgam appears to be formed in accordance with the scheme



and when hydrolysed by means of methyl-alcoholic potassium hydroxide is converted into salts of mixed polycarboxylic acids; these, when distilled, are converted with loss of carbon dioxide into a mixture which consists mainly of two isomeric dicarboxylic acids: one of these melts at 136–137°, and has been definitely identified with a $\beta\beta'$ -dimethyladipic acid which has since been obtained together with its isomerides by the action of copper powder on β -iodobutyric acid:

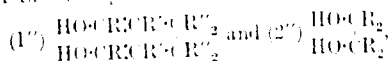


In neither of the two processes was the pure stereoisomeride of the acid melting at 136–137° obtained, but the two eutectics appeared to melt at about 62–65°, and displayed no appreciable difference in behaviour towards solvents. The proportion of the two isomerides obtained from ethylidenemalonate ester varied considerably according as the reduction process was carried out in faintly alkaline or acid solution, respectively.

The coupling at the β -positions of reduced residues has previously been observed when agents such as sodium amalgam or moist aluminium amalgam act on benzylidenacetone, benzylidenebenzylacetone, methylcyclohexenone, and carvene, the products of

such coupling being 1:6-diketones (Harries and others, *Ber.*, 1896, 29, 380; 1898, 31, 1806; *Annalen*, 1904, 330, 235; Stoermer and Möller, *Diss.*, Restock, 1905, p. 24). Ethyl cinnamate with aluminium amalgam in moist ether similarly yields not only the normal dihydro-derivative, but also a little ethyl $\beta\beta'$ -diphenyl-adipate (Henle, *Annalen*, 1906, 348, 16). Wollemann (*Diss.*, Göttingen, 1913, p. 4 *et seq.*) observed that, whilst as a rule, reduction of $\alpha\beta$ -unsaturated compounds by means of hydrogen in presence of palladium gives almost exclusively the normal dihydro-derivative, traces of the bimolecular products could be detected during the reduction of dibenzylideneacetone by this method. The parallelism between these couplings at β -positions and the formation of pinacols by reduction of saturated aldehydes and ketones is almost self-evident. In both cases, the change may broadly be represented by the expression $2X : 2H \rightarrow X_2H_2$, the usual forms of the molecule X being (1) $OC\dot{R}CR''CR''_2$ and (2) $OC\dot{R}_2$, respectively. The forms always contain carbon atoms with distinct latent polarities, and coupling takes place by union of carbon atoms denoted by \cdot signs.

The mechanism of such reductions has often been discussed, and the theory which perhaps has found most favour is that which assumes the union of a hydrogen atom with the oxygen of the carbonyl group, yielding molecules or residues with a free valency (1') $HO\dot{C}R\dot{C}R''CR''_2$ or (2') $HO\dot{C}R_2$. These residues, which virtually contain trivalent carbon atoms, are supposed to unite by means of these, in pairs, giving rise to

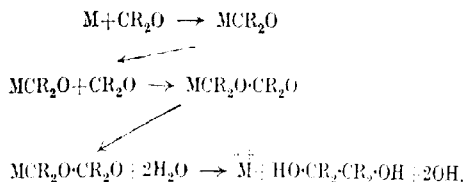


respectively, the former being the unstable end of a 1:6-diketone to which it at once isomerizes.

Such a theory fails to explain why the bimolecular reduction products are only formed when metals in some form are used as reducing agents. This difficulty may no doubt be evaded by assuming that a metallic atom rather than a hydrogen atom become attached to the carbonyl oxygen, and that compounds corresponding with Schlenk's metal ketyls are formed: for example, $NaOC\dot{R}$ rather than $HO\dot{C}R_2$. But the metal ketyls are so highly unstable and the average life of their individual molecules in aqueous or alcoholic solution is consequently so short that the probability of their frequent coalescence in pairs is extremely remote. If, on the other hand, it be supposed that the carbonyl compound is adsorbed on the surface of the metal, then conditions which would admit of ready coupling of the molecules in pairs are provided.

If such adsorption of molecules on the surface be assumed, then coupling might be accounted for in two entirely different modes.

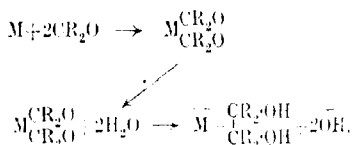
(a) The molecules first adsorbed are attacked by other molecules still in solution; in this manner, two layers of simple molecules one above the other might be formed, these ultimately forming one layer of double molecules by readjustment of electrons in the system which includes both molecules and also the metal and the solvent. The stages assumed may be roughly pictured as follows, where M indicates the mass of metal:



Here some of the metal of course ultimately becomes converted into metal hydroxide or salt.

(b) The individuals of the interacting pairs both form part of the layer of molecules which are directly attached to the metal. These individual molecules lie side by side and with subsequent readjustments of electrons in the system unite in pairs.

Here the supposed stages may be represented as follows:



Whilst hypothesis (b) is perhaps to be preferred to (a) in the present connexion, it is worthy of note that much recent evidence has been accumulating to show that adsorbed layers of gas several molecules thick may occur on the surfaces of solids. It is not altogether unlikely that the natural synthesis of compounds containing carbon chains produced by the concurrence of several simple molecules may in certain cases be traced to localisation and activation of the simple molecules at solid-liquid or liquid-liquid interfaces.

The absence of appreciable quantities of the bimolecular products when hydrogen in presence of metallic catalysts is used as reducing agent finds a ready explanation with the aid of the view, which is widely held, that during such catalytic reductions the first

step consists in the formation of a layer of activated hydrogen on the metallic surface. It is evident that if hydrogen is adsorbed much more rapidly than the reducible compound, the molecules of the latter will come into contact with hydrogen atoms rather than with the metal, and the mechanism for the production of the bimolecular compound will therefore almost wholly be excluded.

On the other hand, Wollemann's observation (*loc. cit.*) that traces of the bimolecular products are formed when dibenzylideneacetone is acted on by hydrogen in presence of palladium can only be harmonised with the preceding suggestions by assuming that catalytic reductions may proceed in two different modes. The more usual mode would involve adsorption of hydrogen, and the other adsorption of reducible compound in the first instance. In this way, it may be possible to reconcile the two hitherto apparently divergent views, each based on experimental grounds, of the mechanism of catalytic reduction processes.

EXPERIMENTAL.

The ethyl ethylidenemalonate was prepared by the condensation of acetaldehyde with ethyl malonate in presence of a small quantity of sodium ethoxide or piperidine, the product being worked up by repeated washing with water, drying, and fractionation in a vacuum.

Reduction of Ethyl Ethylidenemalonate with Hydrogen in Presence of Colloidal Palladium. The ester (5 grams) was dissolved in a mixture of alcohol (20 c.c.) and water (25 c.c.) to which were added 2 c.c. of an approximately 4 per cent. solution of palladium chloride, then 0.1 gram of gum arabic dissolved in water and a little colloidal palladium solution which had been previously prepared. The containing flask, provided with a well-fitting cork and stirrer, was connected with a reservoir containing purified hydrogen, by means of which the air in the flask was first replaced by hydrogen, and interaction was then effected by efficient stirring. Fairly rapid absorption of hydrogen took place even when, as sometimes happened, the catalyst separated from solution as dark, flocculent masses. In the course of about two hours, reduction was as a rule complete, when the flask was detached and its contents were diluted with water and extracted with ether. The extract, recovered by evaporation of the dried etheral solution, was fully saturated and distilled practically constantly at 203–765 mm. It was nearly pure ethyl ethylidenemalonate and on hydrolysis with alkali yielded ethylmalonic acid melting at 109–111°, and decomposing at 160° with formation of carbon dioxide and *n*-butyric acid (Equivalent of the ethylmalonic acid found, 66.6; calculated, 66.0).

Reduction of Ethyl Ethylidenemalonate with Sodium Amalgam.—The ester (15 grams), dissolved in dilute alcohol (20 c.c.), was cooled in a freezing mixture and shaken with successive quantities of well-washed, 1·5 per cent. sodium amalgam (400 grams), the approximately neutral reaction of the alcoholic solution being maintained by frequent additions of acetic acid. Later, complete reduction was as far as possible insured by shaking the solution with washed, 4 per cent. amalgam (100 grams). On subsequently diluting with water, acidifying, and extracting with ether, an oil was obtained which when boiled with methyl-alcoholic potassium hydroxide for two and a half hours yielded a small quantity of a neutral ketone, volatile in steam, and an alkaline mixture of sodium salts.

The ketone, after distillation with steam, was collected. It had a peppermint-like odour and was converted by warming with semicarbazide hydrochloride and sodium acetate into a white solid, evidently a semicarbazone, melting and decomposing at 255°. The total quantity of these products obtained during the course of the work was insufficient for satisfactory characterisation or analysis. The mixture of sodium salts obtained by hydrolysing the crude reduction product, when acidified and extracted with ether, gave a mixture of acids which on standing slowly solidified. The acids present were doubtless for the most part the two stereoisomeric *xx'*-dicarboxy- $\beta\beta'$ -dimethyladipic acids; when the mixture was heated at about 160°, carbon dioxide was evolved and the residue, when distilled at 5 mm. pressure, gave about 3 grams of a pale yellow, oily distillate; this slowly became converted into a white solid mixture of acids which melted over a range, the upper limit being 75°. The equivalent of the mixture determined by titration was 85, the number calculated for a dibasic acid, $C_8H_{14}O_4$, being 87.

Repetition of the reduction of ethyl ethylidenemalonate with sodium amalgam, but using excess of sodium bicarbonate instead of acetic acid to minimise alkalinity, gave somewhat similar results; the mixture of dicarboxylic acids, however, now melted over a range the upper limit of which was 128°. The crude acids were washed with carbon tetrachloride, dried, and analysed (Found: C = 54·9; H = 7·8; equivalent, by titration, = 88, 86·5. $C_8H_{14}O_4$ requires C = 55·2; H = 8·0 per cent.; equivalent = 87).

Samples of mixed acids prepared by the above methods and recrystallised several times were collected and exposed on porous earthenware in an oven at 100°; the residue, after recrystallisation from hot carbon tetrachloride, formed well-defined prisms melting fairly sharply at 136–137°, which is probably very nearly the

correct melting point of one isomeride. The portion which was absorbed by the porous earthenware was extracted with carbon tetrachloride; after solidification, this portion, when slowly heated, began to melt at about 63° , which is therefore probably the approximate melting point of the eutectic.

Synthesis of $\beta\beta$ -Dimethylacrylic Acid from β -Iodobutyric Acid.— β -Iodobutyric acid, made by the action of hydrogen iodide on crotonic acid in aqueous solution, was ground up with "reduced" copper powder, and the mixture heated at 160° for four hours. On submitting the product to distillation under a pressure of 4 mm., a fraction passed over between 160° and 190° which solidified when infected with the solid mixture of $\beta\beta$ -dimethyladipic acids prepared from ethyl ethylenemalonate. The solid after one recrystallisation from carbon tetrachloride melted at 124 – 126° , and its equivalent, determined by titration, was 87, or the theoretical value. After exposure on porous earthenware at 100° and recrystallisation of the residual solid from carbon tetrachloride, well-defined prisms melting at 136 – 137° were obtained. By extraction of the earthenware with carbon tetrachloride, a solid was obtained which began to fuse at 62° and closely resembled that from the partly purified mixture of $\beta\beta$ -dimethyladipic acids obtained from the sodium amalgam reduction product of ethyl ethylenemalonate. A mixed melting-point test, applied to the specimens melting at 136 – 137° , confirmed the identity of the acid prepared by the two distinct methods.

The authors' thanks are due to the Advisory Council of the Department of Scientific and Industrial Research for a grant to one of them (L. H.) which made it possible for this work to be done.

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[Received, May 9th, 1923.]

CLXXXII. *The Theory of Acid-Alkali Solution Equilibrium as Applied to Salts of Moderately Strong but Sparingly Soluble Acids.*

By EDMUND BRIDGES RUDHALL PRIDEAUX.

It is well known that titration of the total alkali in salts of very weak acids is carried out with the aid of acid-insensitive indicators of low titration exponent, p_T . The weaker the acid, the higher can be the value of p_T ; thus methyl orange ($p_T = 4$) excludes

carbonic acid from a titration, whilst *p*-nitrophenol ($p_T = 5.5$) excludes boric acid. Acids with a dissociation constant higher than 1×10^{-3} , if present in considerable concentration, cannot be excluded without the use of an indicator of too low a titration exponent, which makes the hydron error too high. If, however, the acid is sparingly soluble, it can be estimated by acidimetric methods, even when the constant is as high as 1×10^{-3} . Although the broad lines of the theory of such titrations have been laid down, they do not appear to have been much tested experimentally. The acids to which the special equations deduced below should apply are those with solubilities of 0.02 mol. per litre or less and constants between 1×10^{-3} and 1×10^{-5} .

Benzoic and salicylic acids only have been examined.

The hydron concentration of a solution of a stoichiometrically neutral benzoate or salicylate is given by the well-known equation of hydrolysis, which is expressed for convenience in the form

$$[H^+] = \sqrt{K_W K_A c} \quad (1)$$

in which K_W is the dissociation constant of water, 1×10^{-14} at 23° , and c is the total concentration of the salt NaA at the end of the titration. By taking logarithms and changing the sign, $[H^+]$ is obtained as the negative of its exponent, $-\log[H^+]$ or p_H :

$$2p_H = 14 - \log K_A - \log c$$

In the case of benzoic acid, $K = 6.86 \times 10^{-5}$, so that for a normal solution of sodium benzoate ($c = 1$), for a solution of benzoic acid saturated at 25° ($c = 0.0266$), and for 0.01N-benzoic acid the values of p_H are 9.155, 8.58, and 8.08, respectively. All these values are within the range of phenolphthalein.

The exact neutralisation of salicylic acid can be effected with neutral-red or other neutral-point indicator. The salt is not alkaline to phenolphthalein, and according to Kolthoff a solution containing 1 part of the salt in 10 parts of water is made alkaline by 0.1 c.c. of N_{10} -alkali. The application of the simple equation to salicylic acid in its saturation concentration, 0.0162 mol. per litre at 25° , leads to the values $p_H = 7.6$ and $[H^+] = 2.5 \times 10^{-8}$. For the salt in normal concentration, $p_H = 8.6$ and $[H^+] = 2.5 \times 10^{-9}$. At the latter concentration, therefore, the solution should be just alkaline to phenolphthalein, and be made acid by mere dilution.

This is not the case, and the cause of the discrepancy is the phenolic hydroxyl group, the hydrogen atom of which is free to dissociate when the carboxylic hydrogen atom has been replaced by sodium. The second dissociation constant may be put equal to that of methyl salicylate, 1×10^{-11} . The acidity due to a normal solution of the phenolic anion, HA' , dissociating into H^+ .

and A'' may be calculated as $[H'] = 3 \times 10^{-6}$, which is greater than that of phenolphthalein. Also the quantity of alkali that must be added to bring p_H to a value, 8.4 ($[H'] = 2.5 \times 10^{-9}$), at which the solution will give a decided pink colour with phenolphthalein, can be calculated.

The quantity, x , of added alkali may be put equal to the concentration of the phenolic anion A'' in the equation $[H'] = Kc/[A'']$. Therefore, $x = 2.5 \times 10^{-3}$ or 0.25 c.c. of 0.1N-alkali must be added to 10 c.c. of N-sodium salicylate in order to make $p_H = 8.4$, or, in general, since $x/c = K/[H']$, the over-titration at this end-point will be 0.4 per cent. of the total salicylic acid present.

The distinctive feature of the method of analysis described below is the titration of the strong mineral acid, leaving out of account the weak acid. The end-point at which all the organic acid is free is given approximately by the ordinary dissociation constant of the acid at its saturation or lower concentration: $[H'] = \sqrt{Kc}$.

Benzoic acid: $K = 6.86 \times 10^{-5}$; $c = 0.0276$ at 25°; $[H'] = 1.37 \times 10^{-3}$; $p_H = 2.86$.

Salicylic acid: $K = 1 \times 10^{-3}$; $c = 0.0162$ at 25°; $[H'] = 4 \times 10^{-3}$; $p_H = 2.4$.

If the organic acid is precipitated and washed free from the inorganic acid at a temperature of about 15°, its concentration will be found to be about 0.01; the corresponding values of $[H']$ and p_H are, for benzoic acid, 8.3×10^{-4} and 3.1, and for salicylic acid, 3.16×10^{-3} and 2.5, respectively.

The titration exponents of the indicators chosen should be as near as possible to these points.

Benzoic Acid and Benzoates.

The principal indicators which change colour at or near the calculated p_H of 0.01N-benzoic acid are methyl-orange, dimethyl-yellow, bromophenol-blue, and congo-red.

Methyl-orange, according to Sorensen, changes its colour between p_H 3.1 and 4.4. The initial change from the full acid colour corresponds almost exactly to the hydrogen exponent of 0.01N-benzoic acid, and experience showed that if titration were stopped when the pink colour began to fade or the first trace of orange appeared, the difference between the methyl-orange and the phenolphthalein titration values agreed well with the quantity of benzoic acid extracted by chloroform. It is, however, not easy to detect these faint differences of colour, even with the aid of a comparison solution of $p_H = 3$. The titration exponent, or point of optimum colour change of methyl-orange is 4.0 or 4.2, at which point the mineral acid is overtitrated and the benzoic acid is partly neutralised. The

best conditions for obtaining a sharp end-point are those in which a small fraction of the benzoic acid is neutralised, because the gradient dp_H/dx has its greatest value at the beginning of the neutralisation of a weak acid, that is, one with a dissociation constant less than 1×10^{-3} . This is proved by numerous titration curves, selected examples of which are given in the author's book on "Indicators." A calculation similar to that given below shows that, at $p_H = 4.0$, about 40 per cent. of the benzoic acid is neutralised, and the value of dp_H/dx is now lower than the maximum, as is always the case near the middle of the neutralisation curve of an acid. The useful exponent for this titration will be between $p_H = 3$ and $p_H = 4$; in what follows it has been taken as 3.5 ($[H^+] = 3.16 \times 10^{-4}$).

For the pure acid at $c = 0.01$, the more exact value of $[H^+]$, obtained from the equation

$$[H^+]^2 + [H^+]K - Kc = 0 \quad \dots \quad (2)$$

is 8×10^{-4} . The degree of dissociation or "ion fraction," α , of the acid is given by

$$\alpha = [H^+] / c = 0.08, \text{ and } (1 - \alpha) \alpha = 11.5.$$

By using an approximate calculation into which the total concentration does not enter, the relation

$$(1 - \alpha) \alpha = [H^+] / K = 8 \times 10^{-4} / 6.86 \times 10^{-5} = 11.7 \quad \dots \quad (3)$$

is obtained. Suppose now that alkali is added until the fraction x of the acid is neutralised, and $[H^+]$ is diminished to 3.16×10^{-4} . If α is the "ion fraction" in the modified sense, which includes anion derived from the sodium salt, then

$$(1 - \alpha) \alpha = 3.16 \times 10^{-4} / 6.86 \times 10^{-5} = 4.6, \text{ and } \alpha = 0.176.$$

Of the total anion, αc or $[A^-]$, which is present in one litre of a c -normal solution, an amount equivalent to $[H^+]$ is derived from the free acid still present, and the remainder, $\alpha c - [H^+]$, is equivalent to the salt present, that is, to the quantity of alkali ($[Na^+]$) combined with organic acid at this acidity. In this case, $\alpha c - [H^+] = 0.00176 - 0.000316 = 0.00144 = [Na^+]$. The amount of free acid is $c - [Na^+]$ or 0.00856. The fraction x of the benzoic acid which is neutralised is given by $(1 - x) x = 0.00856 / 0.0144$. The quantity of acid neutralised is therefore 14.4 per cent., and the amount in the free state is about 86 per cent.

Bromophenol-blue (p_H 3.0 to 4.6) is a better indicator than methyl-orange, because the first change is more noticeable, and the titration exponent is lower. The transition tints are peculiar and easy to recognise. Starting from the full yellow of the acid solution, the change is through brownish-yellow to greenish-yellow, which is the

colour given by a solution of sodium chloride of the same concentration as that formed in the titration and saturated with benzoic acid. If the solution is only half saturated, the next colour, bluish-brown, will be obtained. This changes to purple and finally to the blue of the alkaline solution. The titration exponent may be found by Noyes's rule ("Theory of Indicators," p. 172) by subtracting 0.5 unit of p_H on the side of weaker colour (in this case towards the yellow) from the point of half-way change, p_T (in this case 3.9). The titration exponent, p_T , obtained in this way is 3.4, and the corresponding colour was determined by the aid of the mixed acid rectilinear buffer solution already described (*Proc. Roy. Soc.*, 1916, [A], 92, 466). This mixture, when 20 per cent. neutralised ($p_H = 3.44$), has a green colour, or brown when viewed through deep layers. When an additional 0.325 c.c. of 0.2N-alkali is added to 25 c.c. of the mixture, the colour changes to green (purplish-brown through deep layers), and the value of p_H calculated from the formula is 3.59. The addition of 0.65 c.c. of the alkali produces a blue colour, at $p_H = 3.74$. These colours appear different, but are still distinctive, when viewed by electric light.

Salicylic Acid.

The high dissociation constant of salicylic acid places it at the limit of those acids which can be excluded from a titration without introducing an unduly large error in the estimation of the hydric concentration. The hydric concentration calculated from equation (2) above is 3.43×10^{-3} ($p_H = 2.47$) at $c = 0.016$, and 2.7×10^{-3} ($p_H = 2.57$) at $c = 0.01$, which is the average concentration in a filtrate from the solid acid at about 15%. Such indicators as thymol-blue ($p_H = 1.2$ to 2.8) and tropaeolin OO ($p_H = 1.3$ to 3.2) should allow the salicylic acid to be excluded from titration, but a sharp end-point is not to be expected.

The range of tropaeolin OO, according to Kolthoff, is p_H 1.3 to 3.2, with a titration exponent of 2.8. According to Sorensen, the range is from 1.4 to 2.6 and the titration exponent, calculated by Noyes's rule (*vide supra*), is 2.5.*

In 0.001N-hydrochloric acid, tropaeolin OO is yellow, in 0.01N-salicylic acid it is tawny-yellow, and in the saturated solution it has a redder tinge; judged by the effect produced by the unsaturated solution of salicylic acid, therefore, the value of p_T , if this corresponds to a tawny-yellow colour, is 2.5 or even less. If p_T is taken

* These differences may depend on the method of finding the range, whether the eye is aided by a series of colour matches, for example, ferric chloride and cobalt nitrate, or judges the limiting colours without such assistance.

as equal to 2.8 ($\{H^+\} = 1.6 \times 10^{-3}$), equation (3) gives $\alpha = 0.38$, and therefore $\{Na^+\} = \alpha c - \{H^+\} = 0.0022$. Therefore $1 - \alpha$ is 0.0078, or 80 per cent. of the acid is free at this end-point. A difficulty is encountered here whichever way the facts are regarded. If methyl-orange is used at $pH = 3.5$, it may be calculated that 73 per cent. of the salicylic acid is neutralised, 27 per cent. only being free. One of the intermediate tints of methyl-orange cannot be selected because the composition of the solution will then be too near to the point at which the salicylic acid is half neutralised, and the neutralisation curve is too flat (*vide supra*).

A solution containing 10 milliequivalents of sulphuric acid and 0.81 milliequivalent of salicylic acid in 100 c.c. was extracted with chloroform. The aqueous solution was found to contain 9.9 milliequivalents of sulphuric acid, and the chloroform solution 0.72 milliequivalent of salicylic acid. In another 100 c.c. of the solution, the phenolphthalein titration value was 10.8 c.c. and the methyl-orange value (colour change to orange) 10.4 c.c. The fraction of salicylic acid remaining free at the latter point was therefore 0.5.

A solution containing 2.66 milliequivalents of hydrochloric acid and 0.54 milliequivalent of salicylic acid was titrated with 0.2 N-alkali, of which the following quantities (c.c.) were required:

With tropaeolin OO, reddish-orange (i) 12.2 (ii) 11.8.
tawny-orange (i) 13.5 (ii) 13.3.

With phenolphthalein. 16.0.

The difference (16.0 - 13.4) multiplied by 0.2 = 0.52, and this value, obtained when the titration has been carried to the stage corresponding to the tawny-yellow colour of the indicator, agrees with the result to be expected on the assumption that $pT = 2.5$. A continuation of the titration until the colour of the indicator was full yellow gave a figure corresponding to that required for $pH = 2.8$.

Conditions of Equilibrium in the Presence of a Sparingly Soluble Acid.

If a strong acid is to be titrated in the presence of an excess of a weak, sparingly soluble acid, the end-point will not be quite the same as that in the case already considered. The equations are different, because $\{HA\}$, the concentration of the undissociated acid, is now constant, and equal to $c_s - \{H^+\}$, the solubility of the acid itself in water minus the hydron concentration of this solution. In the case of benzoic acid saturated at 25°, $c_s - \{H^+\}$ is about 0.025, whilst it is about 0.01 in the neighbourhood of 15°. Since $\{H^+\}\{A^-\} = K/c_s - \{H^+\}$, then under the above conditions

$$\{A^-\} = 6.86 \times 10^{-5} \{H^+\} \text{ at } 16^\circ \text{ and } 1.7 \times 10^{-6} \{H^+\} \text{ at } 25^\circ.$$

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The concentration of the added alkali, $[\text{Na}']$, which has formed benzoate, is equal to $[\text{A}'] - [\text{H}']$.*

If x is the amount of alkali added in excess of that required to neutralise the hydrochloric acid, and V is the volume of the titrated solution, then

$$x/V = [\text{A}'] - [\text{H}'] = K[\text{HA}]/[\text{H}'] - [\text{H}'] \quad \dots (4)$$

Writing for $K[\text{HA}]$ one of the values given above and choosing $p_H = 3.5$ ($[\text{H}'] = 3.16 \times 10^{-4}$) as the end-point of the titration,

$$x = V(6.86 \times 10^{-7} / 3.16 \times 10^{-4} - 3.16 \times 10^{-4}).$$

Since V is expressed in litres, then, for a titrated volume of 20 c.c.

$$\begin{aligned} 0.02 \times 1.85 \times 10^{-3} &= 3.70 \times 10^{-5} \text{ equivalent} \\ 0.037 \text{ c.c. of normal reagent.} \end{aligned}$$

Similarly for $V = 50$, $x = 0.093$

and for $V = 100$, $x = 0.185$.

The volume is usually about 50 c.c., and therefore the accuracy is about 0.1 c.c. of normal acid or about 0.5 per cent. in a titration of 20 c.c. of normal sodium benzoate.

This result has been applied to the direct titration both of the alkali and of the acid in sodium benzoate. In order to avoid the obscuration due to the precipitated acid, chloroform (about 50 c.c.) is placed in a stoppered 100 c.c. cylinder, the solution (10 to 30 c.c.) of sodium benzoate is added followed by a few drops of bromophenol-blue solution, and the mixture is titrated with N - or $N/2$ -acid until the colour is green or brownish-blue (see below). The volume, V , of the aqueous layer is noted in case a correction is required. To secure the best results, this volume should be kept small; that of the chloroform may be large, and the temperature should be low.†

If a correction is added to the titration value of the total alkali, it must also be added to the subsequent titration value of the benzoic acid. The latter titration is effected by adding standard alkali in the presence of phenolphthalein until a purple tinge is obtained. A single drop of $N/2$ alkali will then give a full red colour, which masks the blue.

* The concentration of the undissociated sodium benzoate can be left out of consideration at these concentrations.

† The titration of total alkali in benzoates and sulcyates in the presence of ether has been briefly described by Kolthoff (*Z. anorg. Chem.*, 1921, 115, 117). In both cases, apparently tropaeolin OO was used and the results, if they refer to salts of theoretical composition, show a slight excess of total alkali.

EXPERIMENTAL.

The solutions to be tested were made either with known amounts of sulphuric or hydrochloric acid and of the organic acid, or by decomposing normal solutions of the commercial organic salts with a known excess of standard acid; in the latter case, the filtrate from the precipitated acid was analysed. The procedure has been worked out in detail so as to afford a method of estimating both the alkali and the acid in the salts, and several checks have been introduced as follows. After filtration, the precipitated acid, benzoic or salicylic, is washed free from the inorganic acid, and the filtrate and washings are titrated first in the presence of an indicator of low titration exponent and then with phenolphthalein. The difference between the two titration values, multiplied by a factor if necessary, corresponds to the quantity of dissolved organic acid, which may be checked by again acidifying the neutralised filtrate, extracting the organic acid with chloroform, and titrating it in the separated chloroform extract. Alternatively, the original filtrate may be extracted with chloroform, and the excess of sulphuric or hydrochloric acid in the extracted aqueous solution estimated; the chloroform extract also is titrated. In both cases, the precipitated organic acid is titrated separately, and the quantity added to that of the dissolved acid, gives the total amount of organic acid. This method, called the chloroform extraction method, was employed to check the composition of solutions of benzoates or salicylates when these had been made from weighed quantities of the salts.

A mixture containing 7.8 c.c. of *N*-sulphuric acid and 1.6 millicquivalents of benzoic acid in 100 c.c. was analysed. After extraction with chloroform, the aqueous solution was found to contain sulphuric acid equivalent to 7.84 c.c. of *N*-acid, the chloroform containing 1.52 millicquivalents of benzoic acid. The extraction was therefore not quite complete.

The differences (in millicquivalents) between the quantities of acid found with the first indicator and of the total acid present are as follows:

First indicator.	Colour change.	Difference.	Difference Total benzoic acid
Methyl orange	Paler red	1.56	0.98
	Orange	1.36	0.85
	Yellow	0.92	0.58
	Brownish-yellow	1.43	0.91
Bromophenol blue	Brownish-yellow	1.43	0.91
	Bluish-brown	1.43	0.91
	Purple	0.85	0.53

A sample of sodium benzoate was decomposed with excess of

standard sulphuric acid. The precipitated benzoic acid was removed and estimated as described above.

The sulphuric and benzoic acids together were equivalent to 9.9 c.c. of *N*-acid, and the benzoic acid alone to 1.0 c.c.

First indicator.	Colour change.	Difference * (c.c. of <i>N</i> -acid).
Methyl-orange	Orange	0.8; 0.84
	Orange-yellow	0.4
Dimethyl-yellow	Pink (first change)	0.9
	Orange	0.7; 0.8
Bromophenol-blue	Green (first change)	1.1
	Bluish-brown	1.0; 1.0
	Purple	0.9; 0.9

* In these experiments, the difference is numerically equal to the ratio difference/total benzoic acid.

These and the preceding results confirm the conclusion that 80 to 90 per cent. of the benzoic acid is free when the colour of the methyl-orange is orange. The change, however, is not very sharp. Bromophenol-blue gives a good end-point, and when its colour is bluish-brown the whole of the benzoic acid is excluded from the titration, a result which is not quite in agreement with calculation.

Into 50 c.c. of a saturated solution of benzoic acid which required 1.0 c.c. of *N*-alkali for neutralisation there was run the equivalent of 5.66 c.c. of *N*-acid. After the addition of a little more solid benzoic acid, *N*-alkali was run in until bromophenol-blue became green, 5.8 c.c. being required. After the addition of 10 c.c. of chloroform, 5.9 c.c. of *N*-alkali were required to produce the same change of colour. The overtitrations, x , of alkali, which forms benzoate, at $\mu = 3.5$ are therefore 0.14 c.c. in the absence of chloroform and 0.24 c.c. in the presence of chloroform.

A normal solution of sodium benzoate was analysed (a) by the chloroform extraction method already mentioned, and (b) by the double titration method in presence of chloroform described above. The results were: in (a), total alkali = 12.1, benzoic acid = 11.5; in (b), total alkali = 12.1, benzoic acid = 11.65.

Another sample of sodium benzoate gave after similar treatment (a) total alkali = 19.25, benzoic acid = 18.55, and (b) total alkali = 19.32, benzoic acid = 18.50.

The total alkali actually present in the volume of benzoate solution taken was found (from the weight of the solid and of the alkali obtained on ignition) to be 19.44. Thus the error calculated above for a volume of 50 c.c., namely, 0.09 c.c. of normal reagent, agrees well with the error found. This correction must be added both to the total alkali and to the benzoic acid titration values.

The samples of sodium benzoate were low in benzoic acid content.

the corrected ratios of alkali to acid being (a) 1.05 and 1.03 (b) 1.04 and 1.04 in the two cases. A sample made from benzoic acid and the calculated quantity of alkali gave: total alkali = 20.1, benzoic acid = 20.0, the corrected ratio being $20.2/20.1 = 1.005$.

Salicylates may be analysed by a similar method in the presence of tropæolin OO, the end-point being taken when the colour of the solution is tawny-yellow or orange or red. The concentration of the salicylic acid extracted by the aqueous solution from the saturated chloroform solution was found to be 0.012 at about 15° and 0.0162 at 25°.

The value of $[H^+]$ corresponding to a mean concentration of 0.0013 is, by equation (4), 3.2×10^{-3} ($pH = 2.5$), and the mean concentration of the undissociated acid is again 0.010. Therefore $K_a[H.A.]$ is 1×10^{-5} . By titrating to an exponent of 2.8, the amount of alkali which still remains as salicylate is $x = 1/(1.0 \times 10^{-5}/1.6 \times 10^{-3} - 1.6 \times 10^{-3}) = 3.65 \times 10^{-3}$.

Thus, at $V = 20, 50$, and 100 c.c., $x = 0.063, 0.23$, and 0.47 c.c., respectively. It is evident from the results that titration to an orange colour agrees most closely with the deficit of standard acid (namely, 0.25 c.c., calculated for $pH = 2.8$). If the titration is continued until the colour is pink, the reading will almost agree with the value of total alkali found by other methods, that is, all the salicylic acid will be free. But $pH = 2.5$ for free salicylic acid. It seems, therefore, either that the salicylic acid thus set free in presence of chloroform is a stronger acid than would be expected from its dissociation constant and its behaviour when shaken with water and chloroform; or that tropæolin OO in these circumstances gives its full acid colour at too low a value of $[H^+]$ (too high a value of pH). The titration of the liberated acid with phenolphthalein gives values higher than those expected. This divergence is scarcely at all due to an error in the choice of the end-point, for, as already shown (p. 1626), such error, which can be diminished by using an excess of phenolphthalein, will then only amount to 0.4 per cent. of the salicylic acid present. It really reveals an incorrectness in the composition of the sample used. This is proved by the last experiment, in which the solution was made from a weighed quantity of the acid and the calculated amount of alkali, and was rendered slightly acid towards phenolphthalein by the addition of two drops of 0.25*N*-hydrochloric acid. It was then analysed by the method under consideration.

The result shows that 0.1 c.c. must still be added to the tropæolin titration value. This amount would also be added to the phenolphthalein titration value were it not that the end-point is 0.4 c.c. too high, or 0.8 c.c. for 20 c.c. of normal salicylate solution. The

two corrections cancel and the phenolphthalein titration value is correct as it stands.

Total alkali found.		Total alkali found by titration with tropæolin OO.	Salicylic acid found by titration with phenolphthalein.
(a) By weight of salt.	(b) By ignition.		
(a) 20.0	(b) 19.7	Orange, 19.2; pink, 19.4.	19.8
"	"	Tawny, 19.0; orange, 19.4;	
"	"	pink, 19.7.	20.2
"	"	19.75 by chloroform extraction	
"	"	method.	19.6
"	"	Pink, 19.7.	20.0
			(much indicator present)
			(20.0 found
			(20.0 taken
	19.98	19.90	

Summary.

Equations have been deduced by which the hydrion concentration may be calculated which occurs at the end-point in the neutralisation of a mixture of a strong acid with a fairly strong but sparingly soluble acid having a dissociation constant not exceeding 1×10^{-3} . The predicted results have been tested experimentally in the case of benzoates and salicylates, and partly confirmed.

Rapid methods have been described for the titration of both total alkali and acid in benzoates and salicylates.

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[Received, April 18th, 1923.]

CLXXXIII. *Mixed Crystals and Double Salts: A Comparison of Systems containing Water, Ammonium Chloride, and a chloride of Manganese, Iron, Cobalt, Nickel, or Copper.*

By ALBERT CHERBURY DAVID RIVETT and FREDERICK WILLIAM JEFFREY CLENDINNEN.

IN previous papers, descriptions have been given of ternary systems having water and ammonium chloride as two components with manganous (T., 1921, 119, 1329; this vol. p. 1344), ferrous, cobaltous, or nickelous (T., 1922, 121, 801), or ferric (this vol. p. 1338) chloride as third component. There is much in common in all these cases, but particularly so in the first four mentioned. An essential part of the manganous system has been very completely investigated between 10 and 70°, and may reasonably be considered to give the type of the series. In every case, there is abundant evidence that ammonium chloride forms mixed crystals with the dihydrate, $MCl_2 \cdot 2H_2O$, of the chloride of the bivalent

metal, and that the extent of mixed crystal formation, or solubility of the one solid in the other, depends on temperature. Over a certain range there are three series of mixed crystals, and hence, in the ternary systems, three curves of solutions. In other words, there are two gaps in the miscibility of the solids NH_4Cl and $\text{M}'\text{Cl}_2 \cdot 2\text{H}_2\text{O}$. One of these gaps (that nearer to pure ammonium chloride) has been shown for the manganous system to diminish with falling temperature and to vanish at a little below 25° . The other gap no doubt vanishes similarly, but under conditions which are metastable owing to the appearance of a higher hydrate of manganous chloride. With ferrous chloride at 70° , one gap has gone and the other is very small; with cobalt chloride at 60° , a complete series of mixed crystals has been followed from NH_4Cl to $\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$. It is, however, in part metastable owing to the formation of a totally different set of more stable mixed crystals throughout a small range of concentration; with nickel chloride, the two gaps are present at 70° , the one being quite small, the other large. One cannot doubt that the relations described in the manganese case are similar to those that would be found on further examination of the other three over appropriate ranges of temperature.

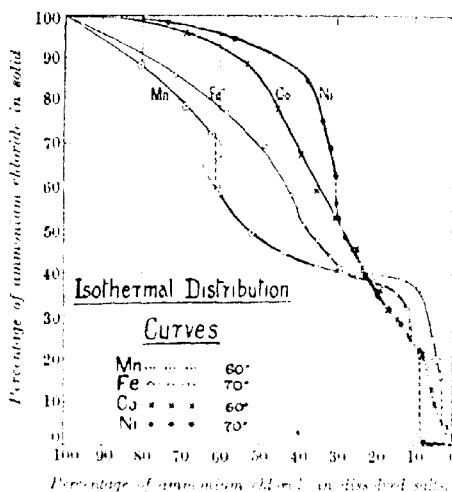
The similarities and contrasts in the systems are most clearly seen in distribution curves where the concentration of one component (ammonium chloride, say) in the solid is plotted against that in the corresponding solution.

In Fig. 1, the ordinates are percentages by weight of ammonium chloride in the solid, whilst as abscissa have been taken the percentages of this salt in the total dissolved matter, regarded as composed of ammonium chloride and the dihydrate of the other chloride. The temperatures are not quite the same in all four cases, but that there is identity of type throughout is obvious. There is, however, another short curve belonging to the cobalt system, not shown in the diagram, which is very nearly horizontal between ordinates 40.0 to 38.4 (ammonium chloride in $2\text{NH}_4\text{Cl} \cdot \text{CoCl}_2 \cdot 2\text{H}_2\text{O}$ equals 39.2 per cent.) and abscissa 29.9 to 20.0 (compare T., 1922, 121, 804, Fig. 2). This shows no connexion whatever with the continuous curve of the same system, the points on which are indicated by crosses: there cannot be a critical point at which the two curves merge. Nothing similar has been found in the other three systems.

The interest of the whole work lies chiefly in the light it throws on the binary systems $\text{NH}_4\text{Cl}-\text{M}'\text{Cl}_2 \cdot 2\text{H}_2\text{O}$. Disregarding the exceptional short series in the cobalt system, it appears that complete miscibility is characteristic of the two solids within certain

temperature limits, outside which limited miscibility occurs in one or both of two regions. This amounts to saying that the thermodynamic potential (ζ -function) of the various possible solid mixtures, ranging from ammonium chloride at one end to $M''Cl_2 \cdot 2H_2O$ at the other, must be a continuous function of the composition, although at certain temperatures one or two portions of it may correspond with metastable systems. The extents of the metastable portions increase with rise of temperature, or, what comes to the same thing, mutual solubility increases with fall in temperature.

FIG. 1.



In practice, one cannot realise the binary liquid phase because of dissociation of hydrates below temperatures of liquefaction, but it has been shown (T₁, 1921, 119, 1336) that it is possible to get some clue to the liquid-solid binary system by a rather forced extrapolation from the ternary. The possible types of these systems may readily be deduced by methods similar to those used by Roozeboom (*Z. physikal. Chem.*, 1899, 30, 385) in the simpler case of mixed crystal formation with one gap. Thus, given that the ζ -function curve for solids is as shown in Fig. 2, i, marked ζ_s , whilst that for the liquids is such as the one marked ζ_l , one can deduce possible binary systems having two eutectics, two transition points or one eutectic and one transition point, according to the ways in which ζ_s and ζ_l cross one another with temperature change.

Fig. 2, sections i to vi, shows, for example, the relations of ζ_s and ζ_L leading to a two-eutectic binary system of the type in the upper part of section xi.

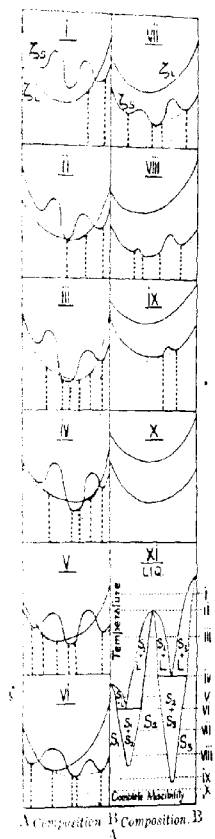
Practical investigation is limited, however, to the solid part of this binary system in which there are five parts marked S_1 , $S_1 + S_2$, S_2 , $S_2 + S_3$, and S_3 , respectively, in Fig. 2, xi, where S denotes a series of mixed crystals. But since the attainment of equilibrium between solids is extremely slow, investigation will be possible only if another component such as water be introduced, and then only if this component enter to but a slight and negligible extent into the compositions of the solid phases. Water appears to be satisfactory from this point of view in the cases dealt with.

The interpretation of the manganous system is that the ζ_L curve changes as shown in Fig. 2, vii to x. At a definite temperature, the regions S_1 and S_2 have merged into one another, that is, the $S_1 \rightarrow S_2$ region of section xi has become closed. Similarly, there is reason to suppose that sooner or later the $S_2 \rightarrow S_3$ region will also vanish, so that complete miscibility is found (section x), a stage already reached in the cobalt system at 60°. It would be of interest to find and examine cases in which the regions $S_1 \rightarrow S_2$ and $S_2 \rightarrow S_3$ open, instead of close, with falling temperature.

The additional short series in the cobalt system introduces a new type. It seems not to be connected in any way with the main continuous series. Two unrelated ζ_s curves will therefore appear in the complete diagram of this system, and their relations to one another and to the ζ_L curve will determine the form of the full temperature-composition diagram of the binary system $\text{NH}_4\text{Cl}-\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$.

Numerous cases are on record in which the regions S_1 , S_2 , and

FIG. 2.



copper by the iodide method, which can be made very accurate by adopting back-titration practice.

TABLE I.
Temperature $25^{\circ} \pm 0.01^{\circ}$.

D_4	Solution.		Residue.	
	NH_4Cl	CuCl_2	NH_4Cl	CuCl_2
1.086	28.02	0.995	73.3	1.51
1.092	27.69	1.78	45.6	24.9
1.093	26.86	2.05	36.1	38.1
1.114	19.59	6.41	34.9	40.0
1.145	15.26	10.96	34.0	49.8
1.191	10.94	16.35	28.9	37.2
1.263	6.53	23.76	27.5	40.2
1.378	3.16	33.2	27.6	44.7
1.524	1.82	43.3	8.08	53.2
—	1.79	43.3	13.64	51.5
1.523	1.41	43.2	0.88	55.2
1.519	—	43.4	—	—

Temperature $0.2^{\circ} \pm 0.1^{\circ}$.

1.078	22.59	0.91	82.4	2.29
1.084	22.28	1.62	41.8	38.6
1.117	13.69	7.57	34.8	42.2
1.178	7.49	15.09	34.9	44.6
1.273	2.95	24.46	32.1	44.6
1.392	1.19	33.86	26.8	45.3
1.495	0.76	41.7	1.70	48.9
1.498	0.75	40.8	0.49	52.6

The part *ab* of Fig. 3 has been established by others and no attempt has been made to fix its limit accurately: the point of present interest is that the tie-lines for the intermediate curve most certainly do not intersect on the composition $2\text{NH}_4\text{Cl} \cdot \text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (marked 2.1.2). It is true that they do not diverge from it very much, but the region *cd* at 25° is by no means negligible. At 0° it becomes greater, being *cc*, an increase with fall of temperature which was to be expected from analogy with the manganese case. S_2 is narrower still. The solution curve is quite short and any deviation in solid phase from $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (*f*) was beyond the limits of accuracy of the methods used.

The system $\text{NH}_4\text{Cl} \cdot \text{FeCl}_3 \cdot \text{H}_2\text{O}$ (*dec. cd.*) is a similar case. $2\text{NH}_4\text{Cl} \cdot \text{FeCl}_3 \cdot \text{H}_2\text{O}$ has been very generally recognised as a compound which could exist in equilibrium with a series of solutions (Rozeboom, *Z. physikal. Chem.*, 1892, **10**, 145; Mohr, *ibid.*, 1898, **27**, 193). Actually there is a clearly defined series of solid solutions round about this composition.

As a matter of fact, it is not possible to have single solids in

The case which is so obvious in the systems described may be supposed to be quite general. Curves such as *a b*, *c d*, and *f* must be finite lengths, although they may be small, and for any binary system where, besides the two components, there are also "molecular compounds" or "double salts" between them, there are two possible points of view suggested by this work. The "molecular

compounds" may represent the last stable intermediate sections of a continuous miscibility curve running from one component to the other. The ξ curve for the solids would be like that of Fig. 4a, with very large gaps and sharp but continuous turning points such as p , q , and r , the tangents from either side almost meeting at these.

On the other hand, it may be that the region $c-d$ in Fig. 3 belongs to a series of mixed crystals totally different from a and f , corresponding with the short series in the cobalt system. In that case the β -figure would be of the type of Fig. 4b.

That a series of solids, when short, should approximate in composition to integral molecular ratios of components is only to be expected. If strain is set up when two solids crystallise together, they are more likely, as a matter merely of symmetrical packing, to mix, if at all, when the components are present in amounts differing but little from simple integral proportions by molecule. The application of the terms "compound" and "double salt" in such limiting cases seems no more justifiable than would be its application to the solid of any particular point occurring in a longer series of mixed crystals, at which components happened also to be in integral ratios by molecule. Investigation of these crystal structures by X-ray diffraction methods would be valuable.

CLXXXIV.—*Hydroxynaphthoic Acids. Part I.*

By FRANK ALBERT ROYLE and JACK ARNOLD SCHEDLER.

OF the seven theoretically possible monohydroxy-derivatives of α -naphthoic acid, only four appear to have been described, namely, 2-hydroxy- α -naphthoic acid, m. p. 158° (Kauffmann, *Ber.*, 1882, 15, 506; Schmitt and Burkhard, *Ber.*, 1887, 20, 2701), 4-hydroxy- α -naphthoic acid, m. p. 183 – 184° (Heller, *Ber.*, 1912, 45, 674), 5-hydroxy- α -naphthoic acid, m. p. 219° (Friedländer, Heilpern, and Spielfogel, *Mitt. tech. Gewerbe. Museums Wien*, 1898, 8, [11 and 12], 316; see also *J. Soc. Chem. Ind.*, 1898, 17, 836), and 8-hydroxy- α -naphthoic acid, m. p. 169° (Ekstrand, *J. pr. Chem.*, 1888, [ii], 38, 278).

In addition to the above, the chemical literature contains references to three other hydroxy- α -naphthoic acids of undetermined constitution. Battershall (*Z. Chem.*, 1872, [iii], 7, 673; *Annalen*, 1873, 168, 144) sulphonated α -naphthoic acid and isolated from the products two isomeric monosulphonic acids which he distinguished by the prefixes α and β . On fusion with potassium hydroxide, the α -sulphonic acid gave a hydroxy- α -naphthoic acid melting at 234 – 237° , whilst the β -sulphonic acid did not yield a pure product.

Stumpf (*Annalen*, 1877, 188, 1) repeated Battershall's work, and in addition to the so-called α - and β -sulphonic acids he isolated a third monosulphonic acid, to which he prefixed the symbol γ . He fused the β - and γ -monosulphonic acids with potassium hydroxide and obtained the corresponding hydroxy- α -naphthoic acids, which melted at 243 – 247° and 186 – 187° , respectively.

The only attempt made by Stumpf to determine the constitution of these hydroxynaphthoic acids was by distillation with lime; he found that the hydroxynaphthoic acid derived from the α -sulphonic acid yielded α -naphthol, whilst those obtained from the β - and γ -sulphonic acids yielded β -naphthol.

Three α -hydroxy- α -naphthoic acids are possible, namely, the 4-, 5-, and 8-hydroxy-acids, and, as has been previously mentioned, all these have been prepared by other and apparently trustworthy methods, and melt, respectively, at 183 – 184° , 219° , and 169° . If we take these melting points as accurate, and there is good reason to believe that they are, then the α -acid of Battershall and Stumpf, which melted at 234 – 237° , was not an α -hydroxy- α -naphthoic acid as they state, but either had a different constitution or was a very impure substance.

Again, Stumpf's β - and γ -acids, being β -hydroxy- α -naphthoic

acids, might be any of the 2-, 3-, 6-, and 7-hydroxy- α -naphthoic acids.

The last three are unknown, and it is scarcely possible that either the β - or the γ -acid could be identical with 2-hydroxy- α -naphthoic acid—which is the only β -hydroxy- α -naphthoic acid that has been described—since the melting points are so widely divergent, and the constitution of this acid is well established.

With these facts in mind, the present authors proposed to prepare the 3-, 6-, and 7-hydroxy- α -naphthoic acids and thus attempt to establish the identity of Stumpf's β - and γ -acids.

Two of the desired acids—the 6- and the 7-hydroxy-acid, were obtained, respectively, from α -naphthylamine-6-sulphonic acid and α -naphthylamine-7-sulphonic acid by diazotising, proceeding through the cyano-sulphonic acid to the carboxy-sulphonic acid and fusing this with potash.

6-Hydroxy- α -naphthoic acid, prepared in this manner, melts at 208–209°, whilst the 7-hydroxy- α -naphthoic acid melts at 253–254°.

3-Hydroxy- α -naphthoic acid was prepared in a similar manner from α -naphthylamine-3-sulphonic acid; it melts at 242–243°.

From a consideration of these melting points it would appear at first sight that Stumpf's β -acid, m. p. 245–247°, might be identical with 3-hydroxy- α -naphthoic acid, m. p. 242–243°. Stumpf, however, describes his β -acid as crystallising from water in bulky masses of needles, a description which agrees perfectly with the characteristics of 7-hydroxy- α -naphthoic acid, m. p. 253–254°.

Stumpf's γ -acid, m. p. 186–187°, might possibly be a very impure specimen of 6-hydroxy- α -naphthoic acid, m. p. 208–209°.

The properties of the α -acid, as previously mentioned, do not appear to suggest those of any of the known α -hydroxy- α -naphthoic acids.

In order to obtain a definite decision on the question, the work of Battershall and of Stumpf has been repeated and the β - and γ -hydroxy- α -naphthoic acids of these workers have been proved to be impure specimens of 7- and 6-hydroxy- α -naphthoic acids, respectively. The α -acid has been definitely found to be pure 5-hydroxy- α -naphthoic acid, the melting point, 219°, of this acid as given by Friedländer, Holpern, and Spielfogel (*loc. cit.*) being incorrect.

EXPERIMENTAL

Materials used. The α -naphthylamine-6- and α -naphthylamine-7-sulphonic acids were commercial products, and these were further purified in the laboratory before use.

α -Naphthylamine-3-sulphonic acid was prepared from the commercial acid sodium salt of α -naphthylamine-3:8-disulphonic acid (C-acid) by boiling with 75 per cent. sulphuric acid for two hours (Kalle & Co., D.R.-P. 64979). On a small scale, it was found advisable to increase the proportion of sulphuric acid recommended in the patent, and 7 parts by weight of 75 per cent. sulphuric acid gave good results without excessive charring.

Diazotisation of α -Naphthylamine-3-, 6-, and 7-sulphonic Acids.

The α -naphthylaminemonosulphonic acid (23 grams) was dissolved in an aqueous solution of sodium bicarbonate (9 grams) and the solution filtered to remove any insoluble impurities. The volumes of water which were found to give the most satisfactory results were 180 c.c., 100 c.c., and 60 c.c. in the case of the 1:7-, 1:6-, and 1:3-acid, respectively. The solution was cooled to about 0°, concentrated hydrochloric acid (65 c.c.) added rapidly, and the finely divided suspension diazotised by the gradual addition of sodium nitrite (7 grams in 20 c.c. of water) with stirring, the temperature being maintained below 5°—this is especially necessary with the 1:6- and 1:7-acids, but with the 1:3-acid the temperature may be slightly higher without the formation of undesirable compounds taking place. The diazonium chlorides separated in the case of the 1:6- and 1:7-acids as light brown, semi-crystalline solids, whilst the 1:3-diazonium chloride was canary-yellow and quite crystalline in character. The solutions were saturated with sodium chloride and filtered. The solid diazonium chlorides were washed with cold saturated salt solution and used in a damp condition.

1-Cyanonaphthalene-3-, 6-, and 7-sulphonic Acids.—The solid diazonium compound was added to a hot cuprous cyanide solution (36–60) prepared in the usual way,* and the mixture was subsequently warmed on the steam-bath for an hour. Concentrated hydrochloric acid was then added to the hot solution, the precipitated cuprous cyanide filtered off, and washed with a little hot water, the washings and filtrate were evaporated to dryness, and the residue was extracted several times with 40–55 per cent. alcohol. The alcohol was evaporated and the nitriles were recrystallised from a small bulk of water, animal charcoal being utilised if necessary.

It was not easy to obtain these nitriles in a sufficiently pure state

* In preparing the cuprous cyanide solution, any unnecessary excess of cuprous cyanide was avoided by adding dilute hydrochloric acid to the α solution until a faint opalescence was detected. Unless this precaution was observed, the cyanosulphonic acids were invariably contaminated by a purple impurity.

for analytical purposes, and they were usually hydrolysed before any analyses were made.

3-, 6-, and 7-Sulpho- α -naphthoic Acids.—The potassium salt of the cyano-sulphonic acid (or the whole of the solution after the precipitation of the cuprous cyanide) was boiled with 10 per cent. aqueous potassium hydroxide until ammonia ceased to be evolved. Any final trace of copper was removed by passing hydrogen sulphide through the boiling, acidified solution, which was then filtered and evaporated until crystals began to appear. On standing, almost the whole of the desired potassium carboxynaphthalenesulphonate crystallised.

The crystalline character of all three potassium carboxynaphthalenesulphonates readily distinguished them from potassium or sodium chloride. They were usually sufficiently pure for the next stage of operations, but could, if necessary, be readily purified by recrystallisation from water.

In the preparation of the salts, of which the following analyses were made, potassium or sodium salts were used throughout so as to avoid the formation of mixed salts.

Sodium 1-carboxynaphthalene-3-sulphonate crystallises from water or dilute acetic acid in small needles (Found: $\text{H}_2\text{O} = 6.3$; $\text{Na} = 7.7$. $\text{C}_{11}\text{H}_7\text{O}_3\text{SNa} \cdot \text{H}_2\text{O}$ requires $\text{H}_2\text{O} = 6.2$; $\text{Na} = 7.9$ per cent.).

Potassium 1-carboxynaphthalene-6-sulphonate crystallises in microscopic needles from water or dilute alcohol (Found: $\text{H}_2\text{O} = 10.9$; $\text{K} = 11.7$. $\text{C}_{11}\text{H}_7\text{O}_3\text{SK} \cdot 2\text{H}_2\text{O}$ requires $\text{H}_2\text{O} = 11.0$; $\text{K} = 12.0$ per cent.).

Potassium 1-carboxynaphthalene-7-sulphonate crystallises from water or dilute acetic acid in slender needles (Found: $\text{H}_2\text{O} = 10.8$; $\text{K} = 11.8$. $\text{C}_{11}\text{H}_7\text{O}_3\text{SK} \cdot 2\text{H}_2\text{O}$ requires $\text{H}_2\text{O} = 11.0$; $\text{K} = 12.0$ per cent.).

Fusion of 1-carboxynaphthalene-3-, 6-, and 7-sulphonates with Potassium Hydroxide.—The finely powdered, anhydrous sulphonate (1 mol.) was added gradually to fused potassium hydroxide at 260° ; after each addition, the temperature was allowed to rise to 260° and the mass was well stirred. Having been finally heated at 280° for about five minutes, the melt was cooled, dissolved in water, and almost neutralised with sulphuric acid, and from the solution, filtered if necessary, the hydroxy- α -naphthoic acid was precipitated by concentrated hydrochloric acid. The crude acid was purified by converting it into the sodium salt, the aqueous solution of which was boiled with animal charcoal and filtered. The hydroxy- α -naphthoic acid was then reprecipitated with hydrochloric acid and recrystallised from boiling water.

6-Hydroxy- α -naphthoic acid is almost insoluble in cold water.

but it is readily soluble in boiling water, from which it crystallises in fine, silky needles melting at 208–209°. It is soluble in alcohol; ether, acetone, or warm glacial acetic acid, but much less soluble in benzene or chloroform. With ferric chloride, the aqueous solution gives a dark brown coloration. Dilute aqueous-alcoholic solutions of the sodium salt show a green fluorescence (Found: C = 70.1; H = 4.3. $C_{11}H_8O_3$ requires C = 70.2; H = 4.2 per cent.). The *acetyl* derivative crystallises in needles from dilute acetic acid or toluene. It melts at 209–210° (Found: C = 67.7; H = 4.4; $CO\cdot CH_3$ = 18.3. $C_{11}H_7O_3(CO\cdot CH_3)$ requires C = 67.8; H = 4.3; $CO\cdot CH_3$ = 18.6 per cent.). The *anilide** is almost insoluble in the usual organic solvents, but may be crystallised from acetic acid, from which it separates in short, glistening needles, m. p. 193–194° (Found: N = 5.5. $C_{17}H_{13}O_2N$ requires N = 5.3 per cent.).

7-Hydroxy- α -naphthoic acid, in general properties, is very similar to the 6-hydroxy-acid. It is, however, less soluble in cold water, from which it crystallises in bulky masses of fine needles, m. p. 253–254°. The ferric chloride coloration and the fluorescence are also very similar to those of the previously described acid (Found: C = 70.1; H = 4.5. $C_{11}H_8O_3$ requires C = 70.2; H = 4.2 per cent.).

The *acetyl* derivative, m. p. 221–222°, crystallises in long, transparent needles from dilute alcohol (Found: $CO\cdot CH_3$ = 18.6. $C_{11}H_7O_3(CO\cdot CH_3)$ requires $CO\cdot CH_3$ = 18.6 per cent.). The *anilide*, m. p. 209–210°, forms small needles from acetic acid (Found: N = 5.1. $C_{17}H_{13}O_2N$ requires N = 5.3 per cent.).

3-Hydroxy- α -naphthoic acid is even less soluble in water than either of the above acids. It crystallises from this solvent in short needles melting at 242–243°. The ferric chloride coloration is reddish-brown and the fluorescence of the dilute aqueous-alcoholic solution of the sodium salt is purple (Found: C = 70.1; H = 4.4. $C_{11}H_8O_3$ requires C = 70.2; H = 4.2 per cent.).

The *acetyl* derivative, m. p. 169–170°, crystallises in long, transparent needles from dilute alcohol (Found: $CO\cdot CH_3$ = 18.2. $C_{11}H_7O_3(CO\cdot CH_3)$ requires $CO\cdot CH_3$ = 18.6 per cent.).

Sulphonation of α -Naphthoic Acid.

In their sulphonations of α -naphthoic acid, Battershall and Stumpf (*loc. cit.*) made use of fuming sulphuric acid of unspecified

* The anilides were prepared according to D.R.P. 293897 (*Chemische Fabrik Grichheim-Elektron*), which describes a modification of Schoepff's method (*Ber.*, 1892, **25**, 2744). The hydroxynaphthoic acid, suspended in toluene, was treated with the requisite amount of aniline, and phosphorus trichloride was slowly dropped into the agitated mixture; the solution was finally boiled so as to complete the reaction.

strength; hence it was impossible to repeat their conditions exactly. Parallel results were, however, obtained by heating α -naphthoic acid (1 mol.) with 98 per cent. sulphuric acid (3 mols.) on the steam-bath for eight hours and converting the product into neutral barium salts by the usual method.

Separation of the α -, β -, and γ -Sulphonic Acids.—Fractional crystallisation of the neutral barium salts failed to yield within a reasonable time more than one pure salt. This salt consisted of well-defined, transparent, hexagonal plates corresponding in general characters with Stumpf's α -salt. Conversion of the material remaining in the mother-liquors into acid barium salts resulted in the separation of the β - and γ -salts, but it was found more expedient to convert the whole of the sulphonic acids into their acid barium salts in the first instance. On evaporation of this solution, the almost insoluble acid barium salt of the γ -sulphonic acid was first deposited—and was obtained pure by recrystallisation from boiling water. Further evaporation of the mother-liquors yielded one or two indefinite fractions of granular material and then two very characteristic fractions crystallising in balls of fine needles; these undoubtedly consisted of the acid barium β -sulphonate, which Stumpf described as crystallising in "soft, voluminous, warty masses." The β -salt also was purified by recrystallisation from boiling water. The mother-liquors of the γ - and β -salts were then made neutral with barium carbonate, and on further evaporation gave a good yield of the neutral α -sulphonate. The intermediate fractions and all mother-liquors were fully investigated and readily resolved into α -, β -, and γ -salts, no traces of other salts being detected.

Conversion of the α -, β -, and γ -Salts into Hydroxy- α -naphthoic Acids.—The neutral sodium salts obtained from the preceding barium salts by the usual methods were fused with excess of potassium hydroxide; the resulting hydroxy- α -naphthoic acids were isolated and purified in the manner described in the earlier part of this paper. In each case, the yields from the fusions were satisfactory and the hydroxy- α -naphthoic acids obtained had the following melting points (the figures in brackets are the m. p.'s recorded by Stumpf): α -acid, m. p. 235–236 (234–237), acetyl derivative, m. p. 202–203; β -acid, m. p. 253–254 (243–247), acetyl derivative, m. p. 221–222; γ -acid, m. p. 208–209 (186–187), acetyl derivative, m. p. 209–210.

From these figures it is clear that the β - and γ -acids obtained by Stumpf were impure specimens of 7-hydroxy- and 6-hydroxy- α -naphthoic acids, respectively.

The α -acid had all the properties of Battershall and Stumpf's

α -acid, although it failed to correspond with any of the three possible α -hydroxy- α -naphthoic acids, all of which had been previously described in the literature. Since 4-hydroxy- α -naphthoic acid cannot be obtained from 4-sulpho- α -naphthoic acid by fusion with potassium hydroxide owing to loss of carbon dioxide, and since 8-hydroxy- α -naphthoic acid readily yields an anhydride, the authors draw the conclusion that the α -acid must be 5-hydroxy- α -naphthoic acid, which had been described as melting at 219° by Friedländer, Heilpern, and Spießfogel (*loc. cit.*). In order to justify this conclusion, a specimen of α -naphthylamine-5-sulphonic acid was converted into 5-hydroxy- α -naphthoic acid by the methods described above. The acid obtained in this way crystallised from hot water in long needles melting at $235\text{--}236^\circ$, and gave an acetyl derivative melting at 202° . Further, the preparation of 5-hydroxy- α -naphthoic acid by Friedländer, Heilpern, and Spießfogel's method again yielded the same acid melting at $235\text{--}236^\circ$, and there can be no doubt whatever that Battershall and Stumpf's α -acid was practically pure 5-hydroxy- α -naphthoic acid.

Summary.

1. 3-, 6-, and 7-Hydroxy- α -naphthoic acids have been prepared and characterised.
2. The sulphonation of α -naphthoic acid with 98 per cent. sulphuric acid at 100° has been shown to produce a mixture of 5-, 6-, and 7-sulpho- α -naphthoic acids.
3. The so-called α -, β -, and γ -hydroxy- α -naphthoic acids of Stumpf and Battershall have been proved to be 5-, 7-, and 6-hydroxy- α -naphthoic acids,* respectively.
4. 5-Hydroxy- α -naphthoic acid melts at $235\text{--}236^\circ$, and not at 219° as previously stated.

The authors desire to express their thanks to Professor Lapworth for his interest in this work.

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(Received May 5th, 1923.)

